THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 16, NUMBER 11 · NOVEMBER, 1948

Bond Energies of Hydrocarbons*

L. GERÖ
University for Technical and Economic Sciences, Budapest, Hungary

(Received February 9, 1948)

The spectroscopical dissociation scheme of CO gives for the heat of sublimation of carbon into ^5S carbon atoms $L_e = 169{,}735$ kcal./mole. This means an 84.58-kcal./mole average bond energy in diamond. The C−H bond energy of the methylene radical is 97.02 kcal./mole, the strength of the paraffinic C−C bond 82.59 kcal./mole, the olefinic double bond C=C is 145.12 kcal./mole. The rupture of successive bonds in methane requires 100.76, 97.36, 97.02, 97.02 kcal./mole.

INTRODUCTION

THE determination of bond energies of organic compounds presupposes in most cases the knowledge of the heat of sublimation of carbon. This value can be given with great accuracy by the aid of the spectroscopical dissociation scheme of the CO molecule, as determined by Schmid and Gerö,[1,2] and enables one to determine important quantities of organic chemistry. An attempt to explain thermochemical data by means of the corresponding heat of sublimation value of carbon was made by Schmid[3] directly after the determination of the dissociation energy of CO, while Schmid and Gerö were able to interpret the results of electronic collision experiments in organic compounds.[4]

In view of the different opinions with respect to the value of the heat of sublimation of carbon, however, the values of bond energies of organic compounds given in the literature are very divergent. It seemed, therefore, worth while to review the subject again, and this paper contains part of this work. In this way, very satisfactory values result with respect to the C−C and C−H bond energies of hydrocarbons, which are also in agreement with the data relating to other organic compounds. In regard to aliphatic hydrocarbons an additivity of bond energies is found within a few percent, while the more recent thermochemical measurements make it possible to follow also the finer deviations from bond additivity. The large resonance energies supposed by some authors do not occur.

In order to obtain data characterizing a single molecule, the ΔHf^0 values of heat of formation at 0°K are used. The theoretical values characterizing bond strengths refer to a vibrationless state and have to be calculated by subtracting half the sum of all vibrational frequencies of the molecular ground state. It is to be noted that calculations with these theoretical bond strengths relating to vibrationless states show an improvement of bond additivity, especially in compounds

* This paper is written by J. G. Valatin on the basis of the notes left by Gerö, and of the memory of some discussions. Most of these notes are dated from 1944, and they had had to form the bases of a larger work. Some of the numerical values have been recalculated according to the more recently available thermochemical data, and these are on the responsibility of the compilator of the article. Results concerning some carbonyl compounds and a critical discussion of the more recent literature are contained in the following two articles.

[1] R. Schmid and L. Gerö, Zeits. f. physik. Chemie (B) **36**, 105 (1937).

[2] R. Schmid and L. Gerö, Physik. Zeits. **39**, 460 (1938).

[3] R. Schmid, Math. és Természettudományi Értesitö **54**, 769 (1936).

[4] R. Schmid and L. Gerö, Math. és Természettudományi Értésitö **56**, 865 (1937); **57**, 637 (1938).

containing also other elements besides carbon and hydrogen.

HEAT OF SUBLIMATION OF CARBON

In identifying the energy height of the observed predissociation at 89620 ± 47 cm^{-1} above the $X^1\Sigma$ ($v=0$, $J=0$) ground state in the CO spectrum with the energy height of the C(^{5}S) $+$O($^3P_0$) atomic term combination,[1,2] the height of the atomic term combination C(^{5}S)$+$O($^3P_2$) is at 89400 cm^{-1}. The dissociation energy of O_2 resulting from band spectra is 40990 cm^{-1}. Using a conversion factor 1 cm^{-1} $=2.8581$ cal./mole, there results by means of these data and the heat of formation[5] of CO at 0°K:

$$\begin{aligned} \text{CO(gas)} &\rightarrow \text{C}(^5\text{S})+\text{O}(^3\text{P}_2)-255.514 \text{ kcal./mole},\\ \text{O}(^3\text{P}_2) &\rightarrow \tfrac{1}{2}\text{O}_2(\text{gas})+\ 58.577,\\ \text{C}(c,\text{ graphite})+\tfrac{1}{2}\text{O}_2(\text{gas}) &\rightarrow \text{CO(gas)}+\ 27.202,\\ \hline \text{C}(c,\text{ graphite}) &\rightarrow \text{C}(^5\text{S})(\text{gas})-169.735 \text{ kcal./mole}. \end{aligned}$$

The heat of sublimation of carbon into ^{5}S atoms is accordingly $L_c=169.735$ kcal./mole at 0°K. This is the value which plays the important part mentioned in the calculation of bond energies of organic compounds, these bond energies being characterized in general by energy values counted from the ^{5}S energy level of carbon, the lowest energy state of the sp^3 configuration of tetravalent carbon being to be taken into account as final dissociation product.

In CO carbon is divalent and the levels of the CO($X^1\Sigma$) ground state converge according to the dissociation scheme quoted to the C(^{1}D)$+$O(^{1}D) atomic term combination, the bond energy of the CO molecule being 233.39 kcal./mole. The dissociation energy of CO counted from the lowest C(^{3}P)$+$O(^{3}P) atomic term combination is 158.91 kcal./mole.

Using for the heat of transition of graphite into diamond[6] $\Delta Hf^0=0.577$ kcal./mole, for the heat of sublimation of diamond into ^{5}S carbon atoms at 0°K there results

$$\text{C}(c,\text{ diamond})\rightarrow\text{C}(^5\text{S})(\text{gas})-169.158 \text{ kcal./mole}.$$

The average bond strength of the carbon-carbon linkage in diamond is

$$[\text{C}-\text{C}]_{\text{diamond}}=169.158/2=84.58 \text{ kcal./mole}.$$

BOND ADDITIVITY AND DEPARTURES FROM BOND ADDITIVITY IN THE PARAFFIN HYDROCARBONS

The heats of formation of the normal paraffins[6] show a regular increase of 3.673 kcal./mole per methylene radical at 0°K beginning from hexane. The variation of the heats of formation of the first members of the series is slightly different, the differences probably to be attributed first of all to the effect of the two methyl radicals at the ends of the chain which interact also with the second next methylene radicals. Apart from this, however, there is an apparent bond additivity.

The knowledge of the value of the heat of sublimation of carbon makes it possible to determine the bond strengths. Slight deviations are found from the average bond strength in isomeric paraffin hydrocarbons, which yield also a measure for the departures from bond additivity. This can be illustrated by an investigation of the interaction of methyl radicals on the same carbon atom in isomeric paraffins.[7]

Forming the differences between the heats of formation of 3-methylpentane and n-hexane, and those of 3-methylhexane and n-heptane, there results in average a difference of 0.34 kcal./mole. Approximately, this can be interpreted as the difference by which the sum of the hydrogen bond energies in a methyl radical exceeds three times the $[\text{C}-\text{H}]_{\text{CH}_2}$ hydrogen bond energy in the methylene radical. With this supposition, the total bond energy of an n-paraffin corresponding to a dissociation into C(^{5}S) and H(^{2}S) atoms is

$$(n-1)[\text{C}-\text{C}]_{n\text{-paraffin}}+(2n+2)[\text{C}-\text{H}]_{\text{CH}_2}+0.68 \text{ kcal./mole}.$$

Adding the value 0.34 kcal./mole to the differ-

[5] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, Bur. Stand. J. Research **34**, 143 (1945).

[6] E. J. Prosen, K. S. Pitzer, and F. D. Rossini, Bur. Stand. J. Research **34**, 403 (1945).

[7] The original calculations were performed without data for the isomeric octanes. Analogous calculations performed with respect to the octanes with slight differences give the same results.

ence of heat of formation of 2-methylhexane and *n*-heptane gives 1.46 kcal./mole as the excess energy of two CH_3 radicals at the end of a paraffin chain; adding 0.34 kcal./mole to the difference of heat of formation of 2,2-dimethylpentane and *n*-heptane gives 3.69 kcal./mole as the excess energy of three CH_3 radicals at the end of the chain. The selected figures are rather characteristic, and the average excess energy of a methyl radical is in this way roughly 0.3, 0.7, 1.2 kcal./mole in the case of 1, 2, or 3 methyl radicals at the end of a paraffin chain. This can be considered also as a measure of the departure from bond additivity in the paraffins.

BOND ENERGIES OF THE PARAFFIN AND MONOOLEFIN HYDROCARBONS

In order to calculate the $[C-H]_{CH_2}$ and the average [C−C] bond energies in the paraffin hydrocarbons, we can use the −30.98-kcal./mole heat of formation value of *n*-hexane, the higher *n*-paraffins yielding the same values. With $L_c=169.735$ kcal./mole and the spectroscopical dissociation energy of H_2, $D(H_2)=36115$ cm^{-1} $=103.22$ kcal./mole there results for *n*-hexane,

$$n\text{-hexane}\rightarrow 6C(^5S)+14H(^2S) \\ -1771.93 \text{ kcal./mole.}$$

From the mentioned increase per methylene radical in the paraffin series

$$2[C-H]_{CH_2}+[C-C]=169.735+103.22 \\ +3.673=276.63 \text{ kcal./mole.} \quad (a)$$

Subtracting five times this equation from the corresponding equation for *n*-hexane

$$5[C-C]+14[C-H]_{CH_2}+0.68 \\ =1771.93 \text{ kcal./mole}$$

gives $4[C-H]_{CH_2}=388.10$ kcal./mole, that is,

$$[C-H]_{CH_2}=97.02 \text{ kcal./mole.}$$

The mean paraffinic C−C bond energy is from Eq. (a)

$$[C-C]=82.59 \text{ kcal./mole.}$$

As to the double bond of the monoolefins, the −2.69 kcal./mole heat of formation value[8] for 1-hexene gives for the difference in bond energies of *n*-hexane and 1-hexene

$$2[C-H]_{CH_2}+[C-C]-[C=C]=103.22 \\ +30.98-2.69=131.51 \text{ kcal./mole,}$$

the same difference resulting also for the higher members of the two series. This relation combined with Eq. (a) gives for the double bond

$$[C=C]=145.12 \text{ kcal./mole.}$$

[8] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, Bur. Stand. J. Research **36**, 559 (1946).

METHANE

With the given values of L_c, $D(H_2)$, and the 15.987-kcal./mole heat of formation of methane there results

$$CH_4\rightarrow C(^5S)+4H(^2S)-392.16 \text{ kcal./mole,}$$

involving a mean bond energy of $392.16/4=98.04$ kcal./mole in methane. According to the preceding the mean hydrogenic bond energy of the methylene radical is 97.02 kcal./mole, the excess energy in the methyl radical being 0.34 kcal./mole. This means for the methyl radical

$$CH_3\rightarrow C(^5S)+3H(^2S)-291.40 \text{ kcal./mole,}$$

and the difference of the bond energies of methane and the methyl radical, the energy required to rupture the fourth hydrogenic bond, is

$$CH_4\rightarrow CH_3+H-100.76 \text{ kcal./mole.}[9]$$

Table I shows the energies required to rupture the different bonds in methane, supposing that the bond energy of the CH radical is identical with $[C-H]_{CH_2}$.

TABLE I. Bond energies in methane.

	Energy required to rupture the bond kcal./mole		Heat of formation into $C(^5S)$ and $H(^2S)$ atoms kcal./mole
First C−H bond	97.02	CH	97.02
Second C−H bond	97.02	CH_2	194.04
Third C−H bond	97.36	CH_3	291.40
Fourth C−H bond	100.76	CH_4	392.16

[9] The striking agreement with the results of G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys. **12**, 469 (1944) is to be noted. They obtained for this value 100.8±1 kcal./mole at 0°K by direct reaction kinetical measurements.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

Dissociation Schemes of Some Carbonyl Compounds

L. GERÖ AND J. G. VALATIN
University for Technical and Economic Sciences, Budapest, Hungary

(Received February 9, 1948)

Dissociation schemes and bond energies are given for formaldehyde, acetaldehyde, acetone, and ketene. The distinction between dissociation term combinations which belong or do not belong to the lowest electronic state of the molecule is stressed, only energies corresponding to the former being in connection with bond energies. The survey of the different energetic possibilities may contribute to a better understanding of photo-chemical processes.

IN the preceding article of Gerö[1] the bond energies of some hydrocarbons were given by the aid of the knowledge of the heat of sublimation value of carbon. These bond energies, together with some spectroscopical and thermochemical data, make it possible to determine the dissociation schemes of some carbonyl compounds, and enable a further examination of observed predissociations, dissociation continua, and photo-chemical effects. The investigation of these dissociation schemes allows also a survey of the energetic possibilities which have to be considered in connection with the corresponding photo-chemical processes and may contribute to the understanding of these processes.

The skeleton of the given dissociation schemes is the work of Gerö. A part of the original interpretations have had, however, to be changed owing to the since available data, and the schemes have been further completed. The responsibility for the greater part of the expressed views devolves, accordingly, on Valatin.

TABLE I.

Process	Q kcal./mole
$C(^3P)\rightarrow C(^5S)$	96.60
$C(\text{graphite})\rightarrow C(^5S)$	169.73
$\frac{1}{2}O_2\rightarrow O(^3P)$	58.58
$H_2\rightarrow 2H(^2S)$	103.22
$CO(X^1\Sigma)\rightarrow C(^5S)+O(^3P)$	255.51
$CO(a^3\Pi)\rightarrow C(^5S)+O(^3P)$	116.97
$CO(a'^3\Sigma)\rightarrow C(^5S)+O(^3P)$	97.23
$\equiv CH\rightarrow C(^5S)+H(^2S)$	97.04[a]
$=CH_2\rightarrow C(^5S)+2H(^2S)$	194.08[a]
$-CH_3\rightarrow C(^5S)+3H(^2S)$	291.39[a]
$CH_4\rightarrow C(^5S)+4H(^2S)$	392.16
$C_2H_6\rightarrow 2C(^5S)+6H(^2S)$	665.51[b]
$C_2H_4\rightarrow 2C(^5S)+4H(^2S)$	531.39[c]

[a] The slightly modified values are given in the following paper of Valatin.
[b] With the ΔHf^0 value of E. J. Prosen, K. S. Pitzer, and F. D. Rossini, Bur. Stand. J. Research **34**, 403 (1945).
[c] With the ΔHf^0 value of J. E. Kilpatrick, E. J. Prosen, K. S.Pitzer, and F. D. Rossini, Bur. Stand. J. Research **36**, 559 (1946).

[1] L. Gerö, J. Chem. Phys. **16**, 1011 (1948).

FORMALDEHYDE

In order to obtain data characterizing a single molecule which can be directly compared with the results of spectroscopical and photo-chemical observations, heat of formation values at 0°K are to be used throughout, and every numerical value is given at this temperature. For the heat of formation of gaseous formaldehyde we use the value adopted by Long and Norrish[2] as a "best value" from data of Delépine and Badoche, and of Wartenberg and Lerner-Steinberg,

$$H_2CO(\text{gas})=C(\text{graphite})+H_2+\tfrac{1}{2}O_2 \qquad -25.3 \text{ kcal./mole},$$

which yields by means of the data given in Table I.

$$H_2CO(\text{gas})\rightarrow 2H(^2S)+C(^5S)+O(^3P) \qquad -356.8 \text{ kcal./mole}.$$

The greater part of the data of Table I is given or quoted in the preceding paper of Gerö.

Using the data of Table I and this 356.8-kcal./mole value for H_2CO, the dissociation scheme of Table II is obtained, in which the energy heights of the different dissociation products are counted from the ground level of the H_2CO molecule. As is seen from the dissociation process (6), the bond energy required to remove the oxygen atom is 162.7 kcal./mole. Supposing from the similarity of the vibrational frequencies that the ground state of the formaldehyde molecule is connected with the $a^3\Pi$-state of CO, the dissociation process (7) is

[2] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. **A187**, 337 (1946).

TABLE II. Dissociation products and dissociation energies of formaldehyde.

	Dissociation products	Energy height kcal./mole
1	$H_2+CO(X^1\Sigma)$	−1.9
2	$H(^2S)+HCO$	~75–85
3	$2H(^2S)+CO(X^1\Sigma)$	101.3
4	$H_2+CO(a^3\Pi)$	136.6
5	$H_2+CO(a'^3\Sigma)$	156.4
6	$=CH_2+O(^3P)$	162.7
7	$2H(^2S)+CO(a^3\Pi)$	239.8

TABLE III. Dissociation products and dissociation energies of acetaldehyde.

	Dissociation products	Energy height kcal./mole
1	$CH_4+CO(X^1\Sigma)$	−1.5
2	$-CH_3+HCO$	≈73–83
3	$H(^2S)+CH_3CO$	—
4	$C(^3P)+2H_2+CO(X^1\Sigma)$	87.7
5	$=CH_2+H_2+CO(X^1\Sigma)$	93.4
6	$=CH_2+H_2CO$	95.3
7	$H(^2S)+CH_2CHO$	~98
8	$-CH_3+H(^2S)+CO(X^1\Sigma)$	99.3
9	$CH_4+CO(a^3\Pi)$	137.0
10	$CH_4+CO(a'^3\Sigma)$	156.8
11	$=CHCH_3+O(^3P)$	~175.1
12	$-CH_3+H(^2S)+CO(a^3\Pi)$	237.8

characteristic of the bond strengths of the hydrogen atoms, and for the mean bond energy of a hydrogen atom the result is 119.9 kcal./mole. This figure contains, however, also the interaction energy of the hydrogen atoms with the oxygen atom. The role of the $CO(a^3\Pi)$ state in formaldehyde is meant in the sense that the vibrational levels of the formaldehyde ground state converge, directly or by a successive convergence of the levels of the H+CHO term combinations, to the energy height of process (7), the corresponding term combination giving also the asymptotic energy value of the potential function of the formaldehyde ground state.*

Accordingly, it is evident that one cannot estimate bond energies from the energy height of the dissociation products (3). In view of the opinions found in the literature, it is to be emphasized that the energy heights of predissociation continua which belong to different electronic states of the molecule, are, in general, not characteristic of the properties of the molecular ground state, and cannot be brought into connection with the concept of bond energies. On the other hand, the energy heights of predissociations play an important part in chemical reactions, and dissociation continua can also get a role by direct transition in the primary absorption process of a photo-chemical decomposition.

The energy height of the dissociation products (2) which play an important part in the photolysis of formaldehyde has been estimated from the energy height (3), by means of the 26-kcal./mole and 16-kcal./mole activation energies of the reaction $HCO \rightarrow H(^2S)+CO(X^1\Sigma)$ given by Gorin[3] and by Style and Summers.[4] As our knowledge with respect to the HCO radical is very little, it cannot be decided whether the low ~75–85-kcal./mole energy value of the dissociation process (2) as compared with the formerly calculated 119.9-kcal./mole mean hydrogen bond energy means merely a strong reorganization energy of the HCO radical—with the opposite sign as in methane where the energy required to remove the first hydrogen atom is 100.8 kcal./mole in spite of a mean bond energy of 98 kcal./mole—or whether the ground state of formaldehyde corresponds to an excited energy state of HCO, in which case process (2) is not characteristic to the ground state of H_2CO, in the same way as process (3) is not. In any case, it is possible that HCO has an excited energy state which should be included in Table II, and which might play a role in the photolysis of formaldehyde.

From the point of view of the formaldehyde photolysis observed between 3650–2600A, the processes (1), (2), and (3) of Table II have to be taken into account. The possibility of process (3) at shorter wave-lengths is to be emphasized, since this process is generally left out of consideration. The predissociation at 2750A observed by Price[5] corresponds also to these dissociation products, though this predissociation limit is often attributed to the removal of a single hydrogen atom.[6] The predissociation observed at 1745A, corresponding to the "extremely diffuse band" of Price, could be attributed, according to Table II, either to the term combination $H_2+CO(a'^3\Sigma)$ or to $=CH_2$

* See also J. G. Valatin, Comptes rendus **226**, 702 (1948).

[3] E. Gorin, J. Chem. Phys. **7**, 256 (1939).

[4] D. W. G. Style and D. Summers, Trans. Faraday Soc. **42**, 388 (1946).

[5] W. C. Price, J. Chem. Phys. **3**, 256 (1935).

[6] See, for instance, M. Burton, J. Chem. Phys. **7**, 1072 (1939).

$+O(^3P)$, the corresponding term combinations occurring also in the dissociation schemes of acetaldehyde and of acetone, in the spectra of which there are, according to Price, also predissociations in the same region. In this connection we can note also the work of Norrish and Noyes,[7] who did not find any evidence for the formation of oxygen atoms in the far ultraviolet photolysis of formaldehyde.

It can also be noted that as is seen from Table I, in the dissociation scheme of CO we have the atomic term combination $C(^3P)+O(^3P)$ about in the same energy height as the $a\,^3\Sigma$-energy level of CO; in this way, at the places where the $CO(a\,^3\Sigma)$ state occurs between the dissociation products in the given dissociation schemes, we have always also a dissociation limit corresponding to this atomic term combination, this being not represented in the corresponding tables.

ACETALDEHYDE

Reducing the 44.0-kcal./mole heat of formation value of acetaldehyde given by Bichowsky and Rossini[8] to 0°K, the data of Table I result for acetaldehyde

$$CH_3CHO \rightarrow 2C(^5S)+4H(^2S)+O(^3P) \qquad -646.2 \text{ kcal./mole.}$$

TABLE IV. Dissociation products and dissociation energies of acetone.

	Dissociation products	Energy height kcal./mole
1	$C_2H_6+CO(X^1\Sigma)$	5.5
2	$CH_4+CH_2=CO$	19.2
3	CH_4+-CH_2CO	—
4	$-CH_3+CH_3CO$	—
5	$H_2+CH_4+C(^3P)+CO(X^1\Sigma)$	79.0
6	$=CH_2+CH_4+CO(X^1\Sigma)$	84.8
7	$=CH_2+CH_3CHO$	86.3
8	$2-CH_3+CO(X^1\Sigma)$	88.2
9	$H(^2S)+-CH_2COCH_3$	~98
10	$C_2H_6+CO(a^3\Pi)$	144.0
11	$C_2H_6+CO(a\,^3\Sigma)$	163.8
12	$=C(CH_3)_2+O(^3P)$	~179
13	$2-CH_3+CO(a^3\Pi)$	226.8

[7] R. G. W. Norrish and W. A. Noyes, Proc. Roy. Soc. **A163**, 221 (1937).

[8] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

TABLE V. Dissociation products and dissociation energies of ketene.

	Dissociation products	Energy height kcal./mole
1	$=CH_2+CO(X^1\Sigma)$	65.6
2	$H(^2S)+CHCO$	~100
3	$=C=CH_2+O(^3P)$	~184
4	$=CH_2+CO(a^3\Pi)$	204.1

This value, together with the data of Table I, enables us to calculate the dissociation scheme of acetaldehyde given in Table III.

With respect to the bond energy of the O atom in acetaldehyde, process (11) gives ~175.1 kcal./mole, where we have made the approximation of identifying the energy required to remove two hydrogen atoms from a methyl radical in ethane with the energy required to the same process in a free methyl radical. The mean bond energy of the methyl radical and the hydrogen atom is from process (12) 118.9 kcal./mole, slightly less than the mean bond energy of hydrogen in formaldehyde. The energy required to remove a hydrogen atom from the methyl radical in process (7) was estimated according to the corresponding value in Table I.

The great variety of the dissociation term combinations (1)–(8) in the region of photolysis is remarkable, all of which can give rise in principle to predissociation effects, and have to be considered in investigating the variation of the absorption and of the acetaldehyde photolysis in function of the wave-length of the absorbed radiation. Though many possibilities of free radical formation can be seen, their role in the chain reactions of the photolysis requires still further investigation. It is not probable that only processes (1) and (2) have to be considered in the acetaldehyde photolysis as it is often supposed in the literature. Also the eventual possibility of free methylene radical formation should be pointed out.

The place of the maximum of the continuous absorption observed by Leighton and Blacet[9] corresponds to the $-CH_3+H(^2S)+CO(X^1\Sigma)$ term combination of process (8). The energy height of the dissociation products (2) has been estimated in the same way as in formaldehyde,

[9] P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).

while the energy of process (3) should be slightly higher.

ACETONE

Using the 427-kcal./mole heat of combustion of liquid acetone, and the values of Table I, we obtain at 0°K

$$(CH_3)_2CO \rightarrow 3C(^5S) + 6H(^2S) + O(^3P) \qquad -926.5 \text{ kcal./mole.}$$

The corresponding dissociation scheme of acetone is given in Table IV.

Process (12) gives for the energy required to remove the oxygen atom ~179 kcal./mole, in the same way as sketched in the case of acetaldehyde, while the mean bond energy of the CH_3 radicals is according to (13) 113.4 kcal./mole.

In the region of the observed photolysis we have again a great variety of term combinations, part of the energetic possibilities being excludable by chemical arguments. It is worth while to mention a work of Herr and Noyes,[10] who point out the eventual importance of the process (8) of the primary formation of two methyl radicals. For processes (3) and (4), the energy heights of which should be estimated from process (8), we have not given estimated values.

KETENE

With a 13.9-kcal./mole heat of formation for ketene, there results

$$CH_2CO \rightarrow 2C(^5S) + 2H(^2S) + O(^3P) \qquad -515.2 \text{ kcal./mole.}$$

Dissociation energies and dissociation products of ketene are given in Table V.

[10] D. S. Herr and W. A. Noyes, J. Am. Chem. Soc. **62**, 2052 (1940).

While for the rupture of the methylenic hydrogen bond we can estimate ~100 kcal./mole, the bond energy of the oxygen atom is about 184 kcal./mole, taking 200 kcal./mole for the energy required to remove the two hydrogen atoms from ethylene, the approximate character of which calculation should, however, be stressed. The rupture of the double carbon bond requires, according to process (4), 204.1 kcal./mole, which energy also contains again the interaction corresponding to the oxygen atom.

At the energy height (1) predissociation should be observed, and this we can identify with the predissociation observed by Norrish, Crone, and Saltmarsh[11] at 3850A ~74.2 kcal./mole. That the transition probability of the predissociation is smaller in the direct proximity of the term combination can be concluded also from the observation of Ross and Kistiakowsky,[12] who reported a photo-chemical decomposition of ketene at 3660A ~78.1 kcal./mole with a decreasing quantum yield as compared with the effect at shorter wave-lengths. According to Burton, Davis, Gordon, and Taylor,[13] the ketene photolysis at $\lambda > 3000$A gives evidence of the formation of free CH_2 radicals which show high reactivity with C_2H_4. Here, it is again to be emphasized that the energy height of a photolysis need not be characteristic to the bond energies, since it may be due also to predissociation effects or to a direct absorption transition into a continuum.

[11] R. G. W. Norrish, H. G. Crone, and O. Saltmarsh, J. Chem. Soc. (1933), 1533.

[12] W. F. Ross and G. B. Kistiakowsky, J. Am. Chem. Soc. **56**, 1112 (1934).

[13] M. Burton, T. W. Davis, A. Gordon, and H. A. Taylor, J. Am. Chem. Soc. **63**, 1956 (1941).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

On the Thermochemistry of Organic Compounds

J. G. VALATIN
*University for Technical and Economic Sciences, Budapest, Hungary**

(Received February 9, 1948)

A discussion of different arguments on the dissociation energy of CO and on the role of the ^5S state of carbon is given. The consistency of the 169.735 kcal./mole value of the heat of sublimation of carbon into ^5S carbon atoms given by Gerö in spite of some arguments of Long and Norrish is shown. The energy required to rupture ethane into two methyl radicals results to be $\{C-C\}_{ethane}=82.78$ kcal./mole, in excellent agreement with the value which can be obtained by a cycle proposed by Van Artsdalen without the use of the heat of sublimation value of carbon. The difference of the mean C−C bond energies in diamond and in the higher members of the paraffin series is 2.04 kcal./mole. The energy required to rupture the double bond in 1-heptene, $\{C=C\}_{1\text{-heptene}}=145.43$ kcal./mole, in 2-methyl-1-butene $\{C=C\}_{2\text{-methyl-1-butene}}=148.70$ kcal./mole. In the acetylene hydrocarbons $\{C\equiv C\}_{1\text{-pentyne}}=198.67$ kcal./mole, $\{C\equiv C\}_{acetylene}=194.28$ kcal./mole.

AS shown in the preceding paper of Gerö,[1] the dissociation scheme of Schmid and Gerö of the CO molecule gives an accurate value for the heat of sublimation of carbon, giving also the cue to many problems on bond energies of organic compounds. Since, however, up to the present this value has not been fully accepted, and the literature contains many different views, further discussion seems necessary. We also try here to reply to the arguments of Long and Norrish,[2] and to make some conclusions with respect to the bond energies in connection with the more recent results of thermochemistry.

DISSOCIATION ENERGY OF CO

The dissociation scheme of the CO molecule[3,4,5] given by Schmid and Gerö in 1936 is based on a fairly great number of spectroscopical observations. There are atomic term combinations at the energy heights 11.55 ev, 11.11 ev, 9.61 ev and 8.87 ev where predissociations were observed. At the heights of the atomic term combinations at 11.11 ev and 10.13 ev term convergences of the $a\,^3\Sigma$ and $I\,^1\Sigma$ levels were observed,[6] at 10.13 ev also a weakening effect at a definite rotational level of the $A\,^1\Pi$ state being present.[5] Besides, the atomic term combinations at 11.55 ev, 8.87 ev, 8.19 ev and 6.90 ev explain the breaking off of emission bands.[4] Some of these effects have no equal independent validity as evidence and may be discussed; the dissociation scheme gives account, however, of such a great variety of observed effects that it seems hardly possible to consider the close agreement of these data with the dissociation scheme of Schmid and Gerö as merely accidental, not even from a purely spectroscopical point of view.

According to this dissociation scheme the CO $X\,^1\Sigma$ ground state dissociates into the $C(^1D)+O(^1D)$ atomic term combination with a bond energy of 10.13 ev. The general acceptance of the dissociation scheme was strongly hindered by the view according to which the ground state of a molecule should dissociate into the atomic ground states. Now it is already known from a great variety of molecules that this is not the case, and the corresponding view cannot be supported either by the results of molecular spectroscopy or by theoretical arguments.[7]

Long and Norrish adduce[8] against the dissociation scheme of Schmid and Gerö that the 6.90 ev dissociation energy of CO finds no place in the empirical relationship of Barrow for the variation of bond strength with internuclear distance in homologous diatomic molecules. They do not take into consideration, however, that in this

* At present Institut Henri Poincaré, Paris, France.
[1] L. Gerö, J. Chem. Phys. **16**, 1011 (1948).
[2] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. **A187**, 337 (1946).
[3] R. Schmid and L. Gerö, Zeits. f. Physik **99**, 281 (1936).
[4] R. Schmid and L. Gerö, Zeits. f. physik. Chemie **B36**, 105 (1937).
[5] R. Schmid and L. Gerö, Phys. Zeits. **39**, 460 (1938).
[6] R. Schmid and L. Gerö, Zeits. f. Physik **106**, 205 (1937).
[7] J. G. Valatin, Proc. Phys. Soc. **58**, 695 (1946).
[8] L. H. Long and R. G. W. Norrish, Nature **158**, 237 (1946).

connection it is not the 6.90 ev energy distance of the $C(^3P)+O(^3P)$ atomic term combination which is to be taken into account, but the 10.13 ev bond energy of the CO ground state corresponding to $C(^1D)+O(^1D)$ which fits rather well to the more recent data of Barrow.[9] In view of the way of determination of the data for the homologous molecules, however, this agreement can only be regarded as support for the calculations with respect to the bond energies of the homologous molecules, and not as a check of the bond energy of CO.

In this connection the close agreement of the bond energy of CO with the bond energy of the $X^1\Sigma_g$ ground state of the isoelectronic N_2 molecule may be remarkable, which latter is according to the determination of Schmid and Gerö[10] 9.76 ev corresponding to a dissociation into the $N(^2D)+N(^2D)$ atomic term combination.

Further support of this dissociation scheme of CO is given by the interpretation of the photochemical decomposition of CO observed by Faltings, Groth and Harteck.[11] An explanation of electronic collision experiments was given according to this scheme by Schmid.[12] Hagstrum and Tate adduce[13] against this interpretation according to their more recent measurements that the observed appearance potential of C^+ ions at 22.8 ± 0.2 ev cannot be due to the $C^+(^4P)+O(^3P)$ term combination which is above this value. Their requirement according to which the appearance potential, if in error, should be higher than the actual dissociation limit, can be satisfied according to a note of Gerö by the $C^+(^2P)+O(^1S)$ term combination at 22.35 ev. The departure is smaller than in O_2 the spectroscopical dissociation scheme of which is generally accepted and where the appearance potential of the O^+ ions at 19.2 ± 0.2 ev is to be interpreted by a dissociation limit at 18.7 ev, and is attributed by Hagstrum and Tate to a potential curve with a maximum of 0.5 ev. The determination of the limit of error of dissociation energy values derived from collision experiments seems to need further investigations.

In connection with the recent note of Hagstrum,[14] according to which the dissociation energy of CO should be 9.6 ev, the predissociation at 9.61 ev corresponding to the $C(^3P)+O(^3P)$ atomic term combination, it can be noted also from the purely spectroscopical side that this scheme cannot account for the observed convergence and predissociation effects at 10.13 ev and the predissociation at 8.87 ev. The hypotesis that the observed predissociation limit at 11.11 ev, which is also a convergence limit of the $a\,^3\Sigma$ levels, should lie 0.25 ev higher than the next atomic term combination, owing to a potential curve with a maximum, seems also to be very improbable on the ground of the observed effects at 11.11 ev.

^5S ENERGY LEVEL OF CARBON

The lowest ^5S energy level of the tetravalent sp^3 configuration of carbon plays an important part in connection with the bond energies of organic compounds, this being the energy level from which bond energies have to be counted probably rather generally. According to some theoretical considerations it is rather the energy differences counted from the energy level of a hypothetical valence state of carbon that are characteristic to the bond strengths of organic compounds.[15,16] These energy differences are, however, by no means observable energy differences and differ essentially from the well-definable bond energies of the chemical bonds. The vibrational levels of the ground state of an organic molecule converge to definite atomic and radical term combinations, defining by successive term convergences of the dissociation products atomic terms which have to be taken into account in connection with the bond energies of the molecular ground state. A given electronic state of a molecule can also be characterized by a potential function which depends only on the coordinates of the atomic nuclei and results by

[9] I wish to express my sincere thanks here also to Dr. Barrow for the kind placing at my disposal of his more recent data. See also Proc. Phys. Soc. **58**, 538, 717 (1946).
[10] R. F. Schmid and L. Gerö, Csillagászati Lapok **6**, 102 (1943).
[11] R. F. Schmid and L. Gerö, Proc. Phys. Soc. **58**, 701 (1946), **59**, 502 (1947).
[12] R. Schmid, Zeits. f. Physik **99**, 274 (1936).
[13] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 534 (1941).
[14] H. D. Hagstrum, Phys. Rev. **71**, 376 (1947). See also H. D. Hagstrum, Phys. Rev. **72**, 947 (1947), in which article the observed effects in the CO spectrum are reviewed, and J. G. Valatin, Phys. Rev. **74**, 350 (1948).
[15] J. H. Van Vleck, J. Chem. Phys. **2**, 20, 297 (1934).
[16] J. Duchesne, P. Goldfinger, and B. Rosen, Nature **159**, 130 (1947).

an averaging of the interactions between all the particles with respect to the fast electronic motions. The asymptotic values of the potential function taken at large internuclear distances also correspond to definite atomic and radical states, and the bond energies are characterized by the energy difference of these asymptotic energy values and of the energy at the place of the minimum of the potential function or of the energy of the lowest discrete energy level of the molecule.

The energy of excitation of the ^5S state of carbon has escaped direct observation by atomic spectra for a long time, and its exact value, 33735.2 cm^{-1}, is only recently known by the measurements of Shenstone.[17] The fact that the $\sim$33800 cm^{-1} value of the ^5S excitation energy of carbon, deduced from the CO dissociation scheme of Schmid and Gerö, represented until its direct determination the best one of the proposed values,[2,8,18] gives further support to the CO dissociation scheme of Schmid and Gerö. It should be also stressed, that though the approximate energy height of the $C(^5S)+O(^3P)$ atomic term combination was indicated for Schmid and Gerö by the older estimated values of Edlén and of Bacher and Goudsmit,[19] after the determination of the CO dissociation scheme the slightly different values[18] proposed by Edlén and by Goudsmit were no more reconcilable with the observed predissociation effects in CO according to the scheme of Schmid and Gerö. We have here, in this way, the rather rare case of molecular spectra having yielded an accurate value for an atomic term distance which had not been until then directly observed in atomic spectra.

As to the remark of Shenstone with respect to the lifetime of the ^5S state of carbon, the question of the metastability of the ^5S state does in no way affect the role, explained above, of the ^5S state in organic compounds, according to which the dissociation limits corresponding to the term convergences and to the asymptotic values of the potential functions should correspond to the ^5S energy state of carbon.

The value of the excitation energy of the ^5S state of carbon seemed to be the most decisive point in the discussion on the heat of sublimation of carbon with Long and Norrish. After the observations of Shenstone, the scheme of Long and Norrish based on Herzberg's CO dissociation energy can no longer be held. In the following, however, we have still to consider the arguments of Long and Norrish which are of thermochemical nature, and to show that they challenge in no way the scheme of Schmid and Gerö.

HEAT OF SUBLIMATION OF CARBON; CONSISTENCY OF THE USED DATA WITH SOME THERMOCHEMICAL ARGUMENTS

According to the paper of Gerö,[1] the dissociation scheme of CO gives together with recent thermochemical data $L_c=L_2=169.735$ kcal./mole at 0°K for the heat of sublimation of carbon into ^5S atoms. The importance of the sublimation heat value corresponding to ^5S carbon atoms in thermochemical calculations has also been stressed by Long and Norrish[2] who have denoted this value with L_2 and pointed out the untenability of some views which do not take into consideration the tetravalency of carbon and the role of the ^5S state.

The direct measurements of the heat of sublimation of carbon show highly divergent results according to the methods used. With the primary process of the carbon sublimation into ^5S carbon atoms, the results of the dynamic experiments which determine the rate of loss in weight of heated carbon filaments are in good agreement with the value deduced from the CO spectrum. The lower value obtained by the equilibrium measurements in the carbon arc has been interpreted by Schmid and Gerö, who constructed also vapor pressure curves which were in good agreement with these measurements,[20] by an equilibrium between ^5S carbon atoms and C_2 molecules. In these calculations Schmid and Gerö used a dissociation energy of 185 kcal./mole for the C_2 molecule into ^5S carbon atoms which they deduced from an extrapolation of the

[17] A. G. Shenstone, Phys. Rev. **72**, 411 (1947).

[18] L. H. Long and R. G. W. Norrish, Nature **157**, 486 (1946); J. G. Valatin, Nature **158**, 237 (1946); B. Edlén, Nature **159**, 129 (1947); and S. Goudsmit, Nature **159**, 742 (1947).

[19] R. Schmid and L. Gerö, Zeits. f. Physik **105**, 36 (1937); B. Edlén, Zeits. f. Physik **84**, 746 (1933); R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934); and see also J. G. Valatin, Comptes rendus **226**, 702 (1948).

[20] R. Schmid and L. Gerö, Mitteilungen der berg- und hüttenmännischen Abteilung der Universität Sopron **9**, 173 (1937).

thermochemical C−C, C=C and C≡C bond energies to a bond with four valencies, a value which could also be somewhat larger in the light of more recent thermochemical data. It should be emphasized that the available spectroscopical evidence on the C_2 spectrum does not at present allow any conclusion as to the dissociation scheme of C_2, and not even the relative position of the singlet and triplet term systems is known. The above state of C_2, if it exists, may be a singlet state, and it may be that all the states of the free C_2 radical correspond to excited atomic states as the states of the free CH radical.[21]

The great divergence of the results of the different carbon heat of sublimation determinations shows in any case the presence of secondary processes, the details of which require further investigations. However, with respect to the interpretation of recent equilibrium experiments as yielding $L_1 \approx 170$ kcal./mole corresponding to a sublimation into ^3P atoms, it should be mentioned that this value, leading to the CO dissociation scheme of Gaydon and Penney,[22,23] seems to be excluded by other observations. One can bring to bear against $D(CO) = 11.11$ ev all the predissociation effects observed below this value and the convergence of the $I^1\Sigma$ terms[6] to about 10.1 ev in the CO spectrum, and the photochemical decomposition process of CO.[11] Besides the spectroscopical and photochemical evidence, in the electronic collision experiments in CO[13] there is an observed appearance potential of O^+ ions at 23.1 ev, whereas the height of the lowest term combination $C(^3P)+O^+(^4S)$ in the scheme of Gaydon and Penney is at 24.73 ev. Thermochemical arguments are also against this scheme since to substitute simply L_1 for L_2 in the present calculations would lead to a faulty theoretical picture. For L_2 the CO dissociation scheme of Gaydon and Penney gives ~267 kcal./mole.

Long and Norrish argue in favor of a higher L_2 heat of sublimation value of carbon also from the results of Andersen, Kistiakowsky and Van Artsdalen[24,25] with respect to the energy required to remove a hydrogen atom from methane. These authors arrive at 100.8 kcal./mole for this energy at 0°K and the striking agreement of this value with the calculations of Gerö[1] show that these measurements can in no way be opposed to the L_2 value given by Gerö. The calculations of Gerö show that the energy required to remove the first hydrogen of methane is slightly greater than the mean bond energy of the hydrogens which results to 98.04 kcal./mole. Long and Norrish suppose the energy required to remove the first hydrogen from methane to be less than the mean bond energy, and conclude from this a larger value of L_2. In regard to their supposition they refer also to theoretical considerations of Van Vleck.[15] Calculations based on the Heitler-London theory, however, cannot be expected to give results which would be able to decide in questions regarding differences of a few percent, or in the improved form given by Voge.[26] Apart from this, the conclusions of Van Vleck do not refer to the former bond energies, but to the "gross energy per bond" which is counted from an energy level corresponding to the hypothetical valence state of the carbon atom.

It is also to be emphasized that the bond energies of the CH_2 and CH radicals occurring in organic compounds is also to be counted from a term combination corresponding to ^5S carbon atoms, as these are given for instance in methane in the paper of Gerö. The bond energy of a CH radical would be accordingly 97.04 kcal./mole[27] corresponding to a $^4\Sigma$ state of CH, and this state of the CH radical cannot be identified with the $CH(X^2\Pi)$ doublet state known from band spectra. In theoretical calculations these two states are often identified, and it is supposed that the dissociation energy of $CH(X^2\Pi)$ is 80 kcal./mole as given by Herzberg. According to the spectroscopical observations of Gerö and Schmid,[21] however, neither of the doublet states of CH are formed from carbon atoms corresponding to

[21] L. Gerö and R. Schmid, Zeits. f. Physik **118**, 210 (1941).

[22] A. G. Gaydon and W. G. Penney, Proc. Roy. Soc. **A183**, 374 (1945); A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, Ltd., London, 1947).

[23] J. G. Valatin, J. Chem. Phys. **14**, 568 (1946), **15**, 336 (1947).

[24] H. C. Andersen and G. B. Kistiakowsky, J. Chem. Phys. **11**, 6 (1943).

[25] G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys. **12**, 469 (1944).

[26] H. H. Voge, J. Chem. Phys. **4**, 581 (1936).

[27] The slight deviation from the value in Gerö's paper is explained later in the text.

energy terms of the lowest s^2p^2 configuration. In this way, it is also doubtful whether CH_2 possesses energy levels lower than the levels of the free methylene radical.

Long and Norrish adduce "three lines of thermochemical evidence" in favor of their energy of excitation value of the ^5S state and of their value for L_2. All the three arguments start, however, from suppositions which do not seem justifiable.

(a) The conclusions concerning the molecular structure of CH_2 are based on Herzberg's mentioned CH dissociation energy value, and refer to an investigation of Burton, Davis, Gordon and Taylor[28] on the photolysis of ketene. The ketene photolysis can be explained satisfactorily by the production of methylene radicals[29] which explanation seems to be preferred also by these authors, and does not involve the attempted consequences.

(b) The stability of the CHO radical fits also into the scheme used throughout this paper.[29] Besides, owing to the interaction of the H atoms with the O atom, the smaller force constant of formaldehyde as compared with methane does not involve a smaller "dissociation energy" of the hydrogen atoms or the missing of an "energy of reorganization" of the CHO radical. The possibility of predissociation effects is also to be emphasized.[29]

(c) Long and Norrish thought to be able to conclude to a lower value of the $C(^5S)$ excitation energy from the fact that according to the observed force constants, bond lengths and ionization potentials the bond strength of CO_2 is smaller than that of CO. But according to the scheme of Schmid and Gerö we have also $CO_2 \rightarrow C(^5S)+2O(^3P)-380.86$ kcal./mole, involving a mean bond strength of 190.43 kcal./mole, compared with the 233.39 kcal./mole bond energy of $CO(X^1\Sigma)$ which corresponds to the dissociation into $C(^1D)+O(^1D)$ atoms. The calculated 162.7 kcal./mole bond energy of the oxygen atom in formaldehyde[29] is again a very reasonable value, and does not make necessary any such conclusions.

[28] M. Burton, T. W. Davis, A. Gordon, and H. A. Taylor, J. Am. Chem. Soc. **63**, 1956 (1941).
[29] L. Gerö and J. G. Valatin, J. Chem. Phys. **16**, 1014 (1948).

BOND ENERGIES

The most important quantity which can be given in order to characterize the strength of a chemical bond is the energy required to dissociate the molecule into definite excited or unexcited atoms and radicals which correspond to the asymptotic energy values of the potential function of the given molecular state. This bond energy is, for instance, for the dissociation of methane into a $H(^2S)$ atom and a free CH_3 radical 100.8 kcal./mole. This is the energy required to rupture the corresponding bond, and the name bond energy is more suitable for the reason that dissociation energy means in spectroscopy the energy height of the corresponding lowest term combination without respect to the possible role of excited atoms or radicals in the molecular ground state. On the other hand, the mean bond energy of the four hydrogen atoms in methane is only about 98 kcal./mole. Owing to the interaction of several atoms, this quantity cannot always be defined with respect to a definite bond, and for instance, the mean bond energy given for the C—O bond in CO_2 includes also an interaction energy of the O atoms and differs considerably either from the average interaction energy between an oxygen atom and the carbon atom, or from the energy required to remove an oxygen atom.

Besides, from a theoretical point of view the energy values characterizing directly the potential function are of greater interest, leaving out of consideration the part of the dynamic effects which are less characteristic of the interaction of the constituent atoms. From this point of view it would also be interesting to know what part of the slight differences in the bond energies of isomeric molecules is due to bonding forces, and what to the differences in the vibrational zero-point energies.

In order to obtain values characterizing a single molecule, besides spectroscopical data we use in the following heat of formation values calculated to 0°K.

PARAFFIN HYDROCARBONS

The evaluation of the results of recent thermochemical measurements allows by the knowledge of the heat of sublimation value of carbon to make some further conclusions with respect to

the bond energies of hydrocarbons. In order to obtain heat of formation differences characterizing a definite bond, we propose to subtract from a given heat of formation value the corresponding values for the hydrocarbon which results by replacing the given radicals with hydrogen atoms.

For instance, the heat of formation differences of 3-methyl-heptane and *n*-heptane, 3-methyl-hexane and *n*-hexane, and 2,4-dimethylhexane and 2-methylhexane give according to the data of Prosen, Pitzer and Rossini[30] equally within a hundredth 3.98 kcal./mole, and this figure is characteristic of the bonds of a methyl radical on the third carbon atom of a paraffin chain. With the same hypothesis as in Gerö's paper that the strength of this methyl bond equals the mean C−C bond resulting from the 3.673 kcal./mole heat of formation difference of successive *n*-paraffins, the 3.98−3.67=0.31 kcal./mole difference is the excess energy of the methyl radical as compared with the bonds in methylene,

$$\Delta CH_3 = \{C-H\}_{CH_3} - [C-H]_{CH_2} = 0.31 \text{ kcal./mole},$$

where $\{C-H\}_{CH_3}$ means the energy required to remove the first hydrogen of the methyl radical. The hypothetical character of this assumption is, however, to be emphasized, leaving a slight uncertainty in the value of the given bond strengths.

In the same way, the difference of heat of formation of 2-methylpentane and *n*-pentane, 2-methylhexane and *n*-hexane, 2-methylheptane and *n*-heptane, 2,4 dimethylhexane and 3-methyl-hexane give almost equally 4.78 kcal./mole, and the difference 4.78−3.67=1.11 kcal./mole can be interpreted as the excess energy because of the second methyl radical at the end of the paraffin chain, the average excess energy per methyl radical being in the case of two methyl radicals 1.11+0.31/2=0.71 kcal./mole.

We have in the *n*-paraffins beginning from hexane,

$$(n-1)[C-C]_{n\text{-paraffin}} + 2(n+1)[C-H]_{CH_2} + 2\Delta CH_3 = nL_c + (n+1)D(H_2) - \Delta Hf^0, \quad (1)$$

$$[C-C]_{n\text{-paraffin}} + 2[C-H]_{CH_2} = L_c + D(H_2) + 3.673 = 276.63 \text{ kcal./mole}, \quad (2)$$

and the two equations give

$$4[C-H]_{CH_2} + 2\Delta CH_3 = L_c + 2D(H_2) - (\Delta Hf^0 + (n-1)\cdot 3.673). \quad (3)$$

The value of the expression in the parenthesis is for the higher *n*-parafins beginning from hexane equally −12.61 kcal./mole, and this gives with $L_c = 169.735$ kcal./mole, $D(H_2) = 103.22$ kcal./mole, $\Delta CH_3 = 0.31$ kcal./mole for $[C-H]_{CH_2}$, the mean bond energy of CH_2 which is supposed to be identical with the energy required to remove a hydrogen atom from a free methylene radical

$$[C-H]_{CH_2} = 97.04 \text{ kcal./mole}.$$

The mean paraffinic carbon-carbon bond strength which contains also the slight interaction of the second next methylene radicals results to be

$$[C-C]_{n\text{-paraffin}} = 82.55 \text{ kcal./mole}.$$

For $n=2$ the analogous equation to equation (1) gives directly the energy required to rupture the bond of the two methyl radicals in ethane. With $\Delta Hf^0 = -16.517$ kcal./mole,

$$\{C-C\}_{ethane} = 82.78 \text{ kcal./mole}.$$

The cycle proposed by Van Artsdalen[31] gives with the 100.8±1 kcal./mole value of Kistiakowsky and Van Artsdalen[24] for the energy of rupture of the first hydrogen atom in methane at 0°K

$2CH_4$	$=2CH_3+2H$	-201.6	kcal./mole
$C_2H_6+H_2=$	$2CH_4$	$+\ 15.46$	kcal./mole
$2H$	$=\ H_2$	$+103.22$	kcal./mole
C_2H_6	$=\ 2CH_3$	$-\ 82.9$	kcal./mole.

The excellent agreement of the two values for $\{C-C\}_{ethane}$ shows again the reliability of the used value of the heat of sublimation of carbon.

It is worth while to note also the relation between the mean $[C-C]_{n\text{-paraffin}}$ bond energy in the higher *n*-paraffins and the mean C−C bond energy in diamond. This can be given by means of the recent thermochemical data independently of the value of the heat of sublimation of carbon. Equation (3) gives

$$2[C-H]_{CH_2} + \Delta CH_3 = L_c/2 + D(H_2) + 6.31 \text{ kcal./mole},$$

[30] E. J. Prosen, K. S. Pitzer, and F. D. Rossini, Bur. Stand. J. Research **34**, 403 (1945).

[31] E. R. Van Artsdalen, J. Chem. Phys. **10**, 653 (1942).

and subtracting this equation from Eq. (2) results

$$[C-C]_{n\text{-paraffin}} = L_c/2 + \Delta CH_3 - 2.64 \text{ kcal./mole.}$$

Since according to Wagman, Kilpatrick, Taylor, Pitzer and Rossini[32]

$$L_{\text{graphite}} - L_{\text{diamond}} = 0.577 \text{ kcal./mole,}$$

$$[C-C]_{\text{diamond}} = L_{\text{diamond}}/2 = L_c/2 - 0.29 \text{ kcal./mole,}$$

$$[C-C]_{\text{paraffin}} = [C-C]_{\text{diamond}} + \Delta CH_3 - 2.35 \text{ kcal./mole.}$$

With $\Delta CH_3 = 0.31$ kcal./mole this gives a difference of 2.04 kcal./mole between the mean carbon-carbon bond energies of the higher members of the paraffin series and of diamond.

MONOOLEFIN HYDROCARBONS

By means of the heat of formation values of Kilpatrick, Prosen, Pitzer and Rossini,[33] we can determine the energy values required to rupture the olefinic double bonds of monoolefins. With the same method as in the case of the paraffins we form the difference

$$\Delta Hf^0_{\text{1-heptene}} - \Delta Hf^0_{n\text{-hexane}} = -6.37 + 30.98 = 24.61 \text{ kcal./mole.}$$

With the approximation that the energy difference of *n*-hexane and the radical formed from 1-heptene by removing the $=CH_2$ radical equals $2[C-H]_{CH_2} + \Delta CH_3$, we get for the energy required to rupture the double bond in 1-heptene

$$\{C=C\}_{\text{1-heptene}} = L_c + \Delta CH_3 - 24.61 = 145.43 \text{ kcal./mole.}$$

By an analogous assumption the energy required to rupture the double bond in 2-methyl-1-butene, in which the remaining paraffin radical also contains two methyl radicals, results using

$$\Delta Hf^0_{\text{2-methyl-1-butene}} - \Delta Hf^0_{n\text{-butane}} = -2.303 + 23.332 = 21.03 \text{ kcal./mole,}$$

$$\{C=C\}_{\text{2-methyl-1-butene}} = L_c - 21.03 = 148.70 \text{ kcal./mole,}$$

which shows a stabilization owing to the interaction of the double bond with the neighboring methyl radical.

ACETYLENE HYDROCARBONS

Using the data of Wagman, Kilpatrick, Pitzer and Rossini,[34] we obtain by the same method the energy required to separate the $\equiv CH$ radical in 1-pentyne.

$$\Delta Hf^0_{\text{1-pentyne}} - \Delta Hf^0_{n\text{-butane}} = 38.90 + 23.33 = 62.23 \text{ kcal./mole}$$

$$\{C\equiv C\}_{\text{1-pentyne}} = L_c + 2[C-H]_{CH_2} - D(H_2) - 62.23 = 198.67 \text{ kcal./mole.}$$

In acetylene

$$\{C\equiv C\}_{\text{acetylene}} + 2[C-H]_{CH_2} = 2L_c + D(H_2) - \Delta Hf^0_{\text{acetylene}}$$

gives with $\Delta Hf^0_{\text{acetylene}} = 54.33$ kcal./mole

$$\{C\equiv C\}_{\text{acetylene}} = 194.28 \text{ kcal./mole.}$$

As it is known from bond lengths and force constants, the C−H bond in acetylene is appreciably stronger than in the paraffins, this example showing clearly again that the sum of the energies required to rupture the different bonds may differ essentially from the heat of formation of the molecule corresponding to a dissociation into the constituent atoms.

ACKNOWLEDGMENTS

At the time of the preparation of these papers, the literature published since the outbreak of the war was not as yet available in Hungary. I wish to express my sincere thanks to all the scientists who made the accomplishment of this work possible by sending reprints of their papers. I am first of all indebted to Mr. Frederick D. Rossini, Chief of the National Bureau of Standards, Washington, for kindly providing me with the great number of their thermochemical papers. I express my thanks to Dr. R. F. Barrow, Professor M. Burton, Dr. R. Cherton, Professor M. Delépine, Professor B. Edlén, Professor G. Herzberg, Dr. J. W. Linnett, Professor R. G. W. Norrish, Dr. H. A. Skinner and Dr. A. D. Walsh.

[32] Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, Bur. Stand. J. Research **34**, 143 (1945).

[33] Kilpatrick, Prosen, Pitzer, and Rossini, Bur. Stand J. Research **36**, 559 (1946).

[34] Wagman, Kilpatrick, Pitzer, and Rossini, Bur. Stand. J. Research **35**, 467 (1945).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

A Tabulation of General Formulas for Inverse Kinetic Energy Matrix Elements in Acyclic Molecules

J. C. DECIUS*
Metcalf Research Laboratory, Brown University, Providence, Rhode Island
(Received April 12, 1948)

In terms of internal coordinates of the bond stretching and bending type, together with a torsional type of coordinate, general formulas for inverse kinetic energy matrix elements have been computed for all 33 possible acyclic configurations involving the given types of coordinates. Tabulations are given both for the general case and for three special cases in which all valence angles of the configuration are assumed to be 90°, 109°28′, and 120°, respectively.

I. INTRODUCTION

GENERAL methods for setting up the secular determinant for molecular vibrations have been given by Wilson[1,2] and by Eliashevich[3] in a form which makes use of internal coordinates adapted to the valence structure of the molecule. Since the transformation from this basis to a basis adapted to the irreducible representations of the group of symmetry operations is now well known, and since methods for performing the numerical solutions of the separate factors of the secular determinant are being facilitated through the use of machines,[4–7] the calculation of the elements of the inverse kinetic energy matrix seems likely to emerge as one of the more laborious steps in the process of computing the vibration frequencies of a molecule. In this connection, it might be mentioned that a recent paper by Wilson[8] provides a scheme whereby the potential energy coefficients can perhaps most conveniently be determined as unknowns to fit a given set of observed frequencies; this method similarly makes use of the inverse kinetic energy matrix.

In view of these facts, a tabulation of general and special algebraic formulas for the inverse kinetic energy matrix elements has been prepared in the hope of reducing the time consumed in calculating normal vibration frequencies. These formulas, which express the result of the transformation from Cartesian to valence-type internal coordinates of small displacements of the atoms from their equilibrium positions, may all be derived from the fundamental formula as given by Wilson,[2]

$$g_{qq'}=\sum_{k=1}^{N}\mathbf{S}_{qk}\cdot\mathbf{S}_{q'k}\mu_k, \tag{1}$$

in which $g_{qq'}$ is a matrix element associated with the coordinates q and q'; $\mathbf{S}_{qk}$ is a vector representing the contribution of the kth atom to the coordinate q, μ_k is the reciprocal mass of the kth atom, and the summation is extended (formally) over all N atoms of the molecule.

Two types of internal coordinates have been principally used to date: the change in distance between two bonded atoms and the change in angle between two bonds having an atom in common. A third type of coordinate is suggested by the resistance to torsion about, e.g., the carbon-carbon bond in ethane. As a general definition of a coordinate of a third type, we adopt the change in dihedral angle between planes of atoms (123) and (234), where neither (123) nor (234) are colinear and where bonds exist between 1 and 2, 2 and 3, 3 and 4. Such a coordinate appears naturally in the C_2 model of H_2O_2, for example.

II. NOTATION AND CLASSIFICATION OF THE INVERSE KINETIC ENERGY MATRIX ELEMENTS

The three types of coordinates described above will be identified by the symbols r, ϕ, and τ

* This work was supported by the Office of Naval Research under Contract N6ori-88, Task Order No. 1.
[1] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939).
[2] E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).
[3] M. Eliashevich, Comptes rendus U.R.S.S. **28**, 605 (1940).
[4] G. K. Carter and G. Kron, J. Chem. Phys. **14**, 32 (1946).
[5] A. A. Frost and M. Tamres, J. Chem. Phys. **15**, 383 (1947).
[6] R. H. Hughes and E. B. Wilson, Jr., Rev. Sci. Inst. **18**, 103 (1947).
[7] W. A. Adcock, Rev. Sci. Inst. **19**, 181 (1948).
[8] E. B. Wilson, Jr., J. Chem. Phys. **15**, 736 (1947).

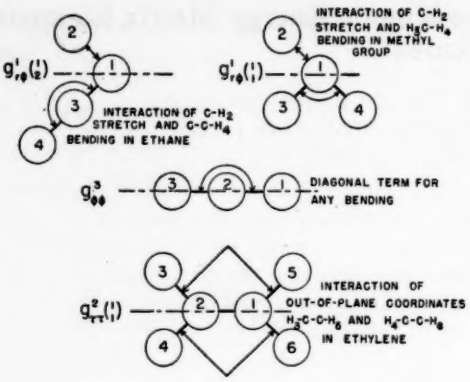

INTERACTION OF C-H2 STRETCH AND H3C-H4 BENDING IN METHYL GROUP
INTERACTION OF C-H2 STRETCH AND C-C-H4 BENDING IN ETHANE
DIAGONAL TERM FOR ANY BENDING
INTERACTION OF OUT-OF-PLANE COORDINATES H3C-C-H5 AND H4C-C-H5 IN ETHYLENE

FIG. 1. Examples of notation.

referring to stretching, bending, and twisting, respectively; thus $g_{r\tau}$ will represent a matrix element involving the interaction of a stretching and a torsional coordinate. Similarly, $\mathbf{S}_{\phi k}$ will represent the contribution of the kth atom to a bending coordinate. The equilibrium configuration of the molecule will define the following set of symbols numerically:

$Q_{ij}=Q_{ji}=$*reciprocal* of equilibrium distance between ith and jth atoms,

$\phi_{ijk}=\phi_{kji}(=\phi_j)=$equilibrium angle between bonds $i-j$ and $k-j$,

$\tau_{ijkl}=\tau_{lkji}(=\tau_{il}=\tau_{li}=$equilibrium dihedral angle between planes of atoms (ijk) and (jkl).

TABLE I. Notations and numbers of distinct configurations for inverse kinetic energy matrix elements in acyclic structure.

q	q'	p	$n^p_{qq'}$	$\binom{C_{q1}}{C_{q'1}}$
r	r	2	1	$\binom{0}{0}$
		1	1	$\binom{1}{1}$
r	ϕ	2	1	$\binom{0}{1}$
		1	2	$\binom{1}{2}$, $\binom{1}{1}$
r	τ	2	2	$\binom{0}{2}$, $\binom{0}{1}$
		1	2	$\binom{1}{3}$, $\binom{1}{2}$
ϕ	ϕ	3	1	$\binom{0}{0}$
		2	2	$\binom{1}{1}$, $\binom{1}{0}$
		1	3	$\binom{2}{2}$, $\binom{2}{1}$, $\binom{1}{1}$
ϕ	τ	3	1	$\binom{0}{1}$
		2	3	$\binom{1}{2}$, $\binom{1}{1}$, $\binom{1}{0}$
		1	4	$\binom{2}{3}$, $\binom{2}{2}$, $\binom{1}{3}$, $\binom{1}{2}$
τ	τ	4	1	$\binom{0}{0}$
		3	2	$\binom{1}{1}$, $\binom{1}{0}$
		2	4	$\binom{2}{2}$, $\binom{2}{1}$, $\binom{2}{0}$, $\binom{1}{1}$
		1	3	$\binom{3}{3}$, $\binom{3}{2}$, $\binom{2}{2}$

As will be seen below, the simplified notation in parentheses will be used, or the subscripts may be omitted entirely, wherever no ambiguity arises. The angles ϕ and τ will have the following ranges: $0<\phi\leq\pi$; $-\pi<\tau\leq+\pi$. The sign of τ is determined through the following convention: viewing the configuration $(ijkl)$ along the line $j-k$, with j nearer the observer than k, let τ be positive if it is traced from the projections of $i-j$ to $l-k$ in the clockwise sense.

Wilson[2] has given expressions for $\mathbf{S}_{rk}$ and $\mathbf{S}_{\phi k}$ (the contribution of the kth atom to the stretching and bending coordinates, respectively) in terms of the above quantities and of unit vectors, $\mathbf{e}_{kl}$, directed from the kth to the lth atom: to these formulas, we now append appropriate expressions for the torsional type of coordinate $(\mathbf{S}_{\tau k})$. It is assumed that the atoms are bonded together in numerical order.

$$\mathbf{S}_{r1}=\mathbf{e}_{21}, \tag{2}$$

$$\mathbf{S}_{r2}=\{12\}\mathbf{S}_{r1}, \tag{3}$$

$$\mathbf{S}_{\phi1}=\frac{Q_{21}}{\sin\phi_2}(\cos\phi_2\mathbf{e}_{21}-\mathbf{e}_{23})=Q_{21}\mathbf{e}_{12}\times\frac{(\mathbf{e}_{12}\times\mathbf{e}_{23})}{\sin\phi_2}, \tag{4}$$

$$\mathbf{S}_{\phi2}=-(\mathbf{S}_{\phi1}+\mathbf{S}_{\phi3}), \tag{5}$$

$$\mathbf{S}_{\phi3}=\{13\}\mathbf{S}_{\phi1}, \tag{6}$$

$$\mathbf{S}_{\tau1}=-\frac{Q_{12}}{\sin\phi_2}\frac{\mathbf{e}_{12}\times\mathbf{e}_{23}}{\sin\phi_2}, \tag{7}$$

$$\mathbf{S}_{\tau2}=\left[\frac{Q_{12}}{\sin\phi_2}-(\cos\tau_{14}\cot\phi_3+\cot\phi_2)Q_{23}\right]\frac{\mathbf{e}_{12}\times\mathbf{e}_{23}}{\sin\phi_2},$$

$$-\cot\phi_3\sin\tau_{14}Q_{23}\mathbf{e}_{23}\times\left(\frac{\mathbf{e}_{12}\times\mathbf{e}_{23}}{\sin\phi_2}\right), \tag{8}$$

$$\mathbf{S}_{\tau3}=\{(14)(23)\}\mathbf{S}_{\tau2}, \tag{9}$$

and

$$\mathbf{S}_{\tau4}=\{(14)(23)\}\mathbf{S}_{\tau1}. \tag{10}$$

In Eqs. (3), (6), (9), and (10) the expression in brackets signifies a permutation of atomic subscripts to be performed upon the previous expression as indicated.

The classification of the matrix elements depends, in the first place, upon the fact that they can be non-vanishing only if the two coor-

TABLE II. General formulas for inverse kinetic energy matrix elements in acyclic structures.

Type	Formula
g^2_{rr}	$\mu_1+\mu_2$
g^1_{rr}	$\cos\phi\mu_1$
$g^2_{r\phi}$	$-\sin\phi Q_{23}\mu_2$
$g^1_{r\phi}(^1_2)$	$\sin\phi_1\cos\tau Q_{13}\mu_1$
$(^1_1)$	$-(\psi^1_{234}Q_{13}+\psi^1_{243}Q_{14})\dfrac{\mu_1}{\sin\phi_{314}}$
$g^2_{rr}(^0_2)$	$-\sin\phi_2\cot\phi_3\sin\tau Q_{23}\mu_2$
$(^0_1)$	0
$g^1_{rr}(^1_3)$	$-\dfrac{\sin\phi_1}{\sin\phi_3}\sin\tau_{24}Q_{13}\mu_1$
$(^1_2)$	$-\sin\phi_{123}\left[\dfrac{\sin\delta^4_{52}}{\sin\phi_{315}}Q_{15}+(\cot\phi_3\sin\tau_{24}-\cot\phi_{315}\sin\delta^4_{52})Q_{13}\right]\mu_1$
$g^3_{\phi\phi}$	$Q^2_{12}\mu_1+Q^2_{23}\mu_3+(Q^2_{12}+Q^2_{23}-2\cos\phi Q_{12}Q_{23})\mu_2$
$g^2_{\phi\phi}(^1_1)$	$\dfrac{\psi^2_{314}}{\sin\phi_{123}\sin\phi_{124}}\left\{Q^2_{12}\mu_1+\left[(Q_{12}-\cos\phi_{123}Q_{23}-\cos\phi_{124}Q_{24})Q_{12}+\dfrac{\cos\phi_{324}\cos\phi_{123}\cos\phi_{124}-\cos^2\phi_{123}-\cos^2\phi_{124}+1}{\psi^2_{314}}Q_{23}Q_{24}\right]\mu_2\right\}$
$(^1_0)$	$-\cos\tau Q_{12}[(Q_{12}-\cos\phi_1Q_{14})\mu_1+(Q_{12}-\cos\phi_2Q_{23})\mu_2]$
$g^1_{\phi\phi}(^2_2)$	$-(\sin\tau_{25}\sin\tau_{34}+\cos\tau_{25}\cos\tau_{34}\cos\phi_1)Q_{12}Q_{14}\mu_1$
$(^2_1)$	$[(\sin\phi_{214}\cos\phi_{415}\cos\tau_{34}-\sin\phi_{215}\cos\tau_{35})Q_{14}+(\sin\phi_{215}\cos\phi_{415}\cos\tau_{35}-\sin\phi_{214}\cos\tau_{34})Q_{15}]\dfrac{Q_{12}\mu_1}{\sin\phi_{415}}$
$(^1_1)$	$[(\psi^1_{435}-\cos\phi_{214}\psi^1_{235})Q_{12}Q_{13}+(\psi^1_{453}-\cos\phi_{214}\psi^1_{253})Q_{12}Q_{15}+(\psi^1_{235}-\cos\phi_{214}\psi^1_{435})Q_{14}Q_{13}+(\psi'_{253}-\cos\phi_{214}\psi'_{453})Q_{14}Q_{16}]\dfrac{\mu_1}{\sin\phi_{214}\sin\phi_{315}}$
$g^3_{\phi\tau}$	$\dfrac{\sin\tau}{\sin\phi_3}Q_{23}[\cos\phi_3(Q_{23}-\cos\phi_2Q_{12})\mu_2-(Q_{34}-\cos\phi_3Q_{23})\mu_3]$
$g^2_{\phi\tau}(^1_2)$	$\dfrac{\sin\phi_{324}\sin\delta^5_{13}}{\sin\phi_{123}\sin\phi_{124}}Q^2_{12}\mu_1+\left[\sin\delta^5_{13}(Q_{12}-\cos\phi_{123}Q_{23})S^{24}_{15}+\dfrac{\cot\phi_4\sin\tau_{15}}{\sin\phi_{123}}[\sin\phi_{324}\cos\delta^5_{13}(Q_{12}-\cos\phi_{123}Q_{23})+\sin\phi_{124}(Q_{23}-\cos\phi_{123}Q_{12})]Q_{24}\right]\mu_2$
$(^1_1)$	$\left[(\cot\phi_{124}\sin\delta^5_{34}+\cot\phi_1\sin\tau_{35})Q_{12}-\dfrac{\sin\tau_{35}}{\sin\phi_1}Q_{15}\right]Q_{12}\mu_1+\left[(\cot\phi_{124}\sin\delta^5_{34}+\cot\phi_1\sin\tau_{35})Q_{12}-\dfrac{\sin\delta^5_{34}}{\sin\phi_{124}}Q_{24}\right](Q_{12}-\cos\phi_{123}Q_{23})\mu_2$
$(^1_0)$	$Q_{12}\left[(\sin\tau_{34}S^{14}_{25}+\cos\phi_1\cot\phi_4\sin\tau_{25}\cos\tau_{34}Q_{14})\mu_1+\dfrac{\sin\tau_{34}}{\sin\phi_1}(Q_{12}-\cos\phi_2Q_{23})\mu_2\right]$
$g^1_{\phi\tau}(^2_3)$	$(\sin\tau_{25}\cos\tau_{34}\cos\phi_1-\cos\tau_{25}\sin\tau_{34})\dfrac{Q_{12}Q_{14}}{\sin\phi_4}\mu_1$
$(^2_2)$	$[(\sin\phi_{214}\cos\phi_{216}\sin\tau_{34}-\cos\phi_{214}\sin\phi_{216}\sin\tau_{36})S^{14}_{65}+\cot\phi_4[(\sin\phi_{214}\cos\phi_{216}\cos\tau_{34}-\cos\phi_{214}\sin\phi_{216}\cos\tau_{36})\cos\phi_{214}-\sin^2\phi_{214}\sin\phi_{416}\sin\tau_{34}\sin\delta^5_{62}]\sin\tau_{56}Q_{14}]\dfrac{Q_{12}}{\sin\phi_{416}}\mu_1$
$(^1_3)$	$[(\sin\phi_{316}\sin\tau_{46}-\sin\phi_{213}\sin\tau_{24}\cos\phi_{216})Q_{12}+(\sin\phi_{213}\sin\tau_{24}-\sin\phi_{316}\sin\tau_{46}\cos\phi_{216})Q_{16}]\dfrac{Q_{13}}{\sin\phi_3\sin\phi_{216}}\mu_1$
$(^1_2)$	$[[\sin\phi_{213}\sin\delta^4_{62}(Q_{15}-\cos\phi_{215}Q_{12})+\sin\phi_{513}\sin\delta^4_{65}(Q_{12}-\cos\phi_{215}Q_{15})]S^{13}_{64}+\cot\phi_3\sin\tau_{46}[\sin\phi_{213}\cos\delta^4_{62}(Q_{15}-\cos\phi_{215}Q_{12})+\sin\phi_{513}\cos\delta^4_{65}(Q_{12}-\cos\phi_{215}Q_{15})]Q_{13}]\dfrac{\mu_1}{\sin\phi_{215}}$

TABLE II.—*Continued.*

Type	Formula
$g^4{}_{\tau\tau}$	$\left(\frac{Q_{12}}{\sin\phi_2}\right)^2\mu_1+\left(\frac{Q_{34}}{\sin\phi_3}\right)^2\mu_4+[(S^{23}{}_{14})^2+\cot^2\phi_3\sin^2\tau Q^2{}_{23}]\mu_2+[(S^{32}{}_{41})^2+\cot^2\phi_2\sin^2\tau Q^2{}_{23}]\mu_3$
$g^3{}_{\tau\tau}(^1_1)$	$\left(\frac{Q_{12}}{\sin\phi_2}\right)^2\mu_1+(S^{23}{}_{14}S^{23}{}_{15}+\cot\phi_{234}\cot\phi_{235}\sin\tau_{14}\sin\tau_{15}Q^2{}_{23})\mu_2+[\cos\delta^1{}_{54}(S^{32}{}_{41}S^{32}{}_{51}+\cot^2\phi_2\sin\tau_{14}\sin\tau_{15}Q^2{}_{23})$ $+\cot\phi_2\sin\delta^1{}_{54}(\sin\tau_{14}S^{32}{}_{51}-\sin\tau_{15}S^{32}{}_{41})Q_{23}]\mu_3$
$(^1_0)$	$\left[(\cot\phi_2+\cot\phi_1\cos\tau_{35})Q_{12}-\frac{\cos\tau_{35}}{\sin\phi_1}Q_{15}\right]\frac{Q_{12}}{\sin\phi_2}\mu_1+\left[(\cot\phi_2+\cot\phi_3\cos\tau_{14})Q_{32}-\frac{\cos\tau_{14}}{\sin\phi_3}Q_{34}\right]\frac{Q_{32}}{\sin\phi_2}\mu_3$ $-[S^{23}{}_{14}S^{21}{}_{35}+\cot\phi_1\cot\phi_3\cos\phi_2\sin\tau_{14}\sin\tau_{35}Q_{12}Q_{32}]\mu_2$
$g^2{}_{\tau\tau}(^2_2)$	$\frac{\psi^2{}_{315}}{\sin\phi_{123}\sin\phi_{125}}\left\{\frac{Q^2{}_{12}}{\sin\phi_{123}\sin\phi_{125}}\mu_1+\left[S^{23}{}_{14}S^{25}{}_{16}+\sin\phi_{325}[\cot\phi_{123}\cot\phi_3\sin\tau_{14}\sin\delta^6{}_{13}S^{25}{}_{16}Q_{23}\right.\right.$ $+\cot\phi_{125}\cot\phi_5\sin\tau_{16}\sin\delta^4{}_{15}S^{23}{}_{14}Q_{25}]+\cot\phi_3\cot\phi_5\sin\tau_{14}\sin\tau_{16}$ $\left.\left.\times\frac{1-\cos^2\phi_{123}-\cos^2\phi_{125}+\cos\phi_{325}\cos\phi_{123}\cos\phi_{125}}{\psi^2{}_{315}}Q_{23}Q_{25}\right]\mu_2\right\}$
$(^2_1)$	$\left[(\cot\phi_1\cos\tau_{36}+\cot\phi_{125}\cos\delta^6{}_{53})Q_{12}-\frac{\cos\tau_{36}}{\sin\phi_1}Q_{16}\right]\frac{Q_{12}}{\sin\phi_{123}}\mu_1-(\cos\delta^6{}_{53}S^{23}{}_{14}S^{21}{}_{56}+\cot\phi_3\cos\phi_{123}\sin\tau_{14}\sin\delta^6{}_{53}S^{21}{}_{56}Q_{23}$ $-\cot\phi_1\sin\tau_{56}\sin\delta^6{}_{53}S^{23}{}_{14}Q_{12}+\cot\phi_1\cot\phi_3\cos\phi_{123}\sin\tau_{14}\sin\tau_{56}\cos\delta^6{}_{53}Q_{12}Q_{23})\mu_2$
$(^2_0)$	$Q_{12}\left[(\cos\tau_{35}S^{15}{}_{26}-\cot\phi_5\cos\phi_1\sin\tau_{35}\sin\tau_{26}Q_{15})\frac{\mu_1}{\sin\phi_2}+(\cos\tau_{35}S^{23}{}_{14}-\cot\phi_3\cos\phi_2\sin\tau_{35}\sin\tau_{14}Q_{23})\frac{\mu_2}{\sin\phi_1}\right]$
$(^1_1)$	$[\cos\delta^3{}_{65}(S^{12}{}_{53}S^{12}{}_{64}+\cot\phi_{123}\cot\phi_{124}\sin\tau_{35}\sin\tau_{46}Q^2{}_{12})+\sin\delta^3{}_{65}(\cot\phi_{123}\sin\tau_{35}S^{12}{}_{64}-\cot\phi_{124}\sin\tau_{46}S^{12}{}_{53})Q_{12}]\mu_1$ $+[\cos\delta^5{}_{43}(S^{21}{}_{35}S^{21}{}_{46}+\cot\phi_{215}\cot\phi_{216}\sin\tau_{35}\sin\tau_{46}Q^2{}_{12})+\sin\delta^5{}_{43}(\cot\phi_{215}\sin\tau_{35}S^{21}{}_{46}-\cot\phi_{216}\sin\tau_{46}S^{21}{}_{35})Q_{12}]\mu_2$
$g^1{}_{\tau\tau}(^3_3)$	$(\sin\tau_{35}\sin\tau_{26}\cos\phi_1-\cos\tau_{35}\cos\tau_{26})\frac{Q_{12}}{\sin\phi_2}\frac{Q_{15}}{\sin\phi_5}\mu_1$
$(^3_2)$	$\left[(\cos\tau_{35}\cos\delta^6{}_{72}-\sin\tau_{35}\sin\delta^6{}_{72}\cos\phi_{215})\frac{Q_{17}}{\sin\phi_{517}}-[\cot\phi_{517}(\cos\tau_{35}\cos\delta^6{}_{72}-\sin\tau_{35}\sin\delta^6{}_{72}\cos\phi_{215})\right.$ $\left.+\cot\phi_5(\cos\tau_{35}\cos\tau_{26}+\sin\tau_{35}\sin\tau_{26}\cos\phi_{215})]Q_{15}\right]\frac{Q_{12}}{\sin\phi_2}\mu_1$
$(^2_2)$	$\left\{\frac{\cos\phi_{214}\cos\phi_{617}-\cos\phi_{217}\cos\phi_{416}}{\sin\phi_{216}\sin\phi_{417}}S^{12}{}_{63}S^{14}{}_{75}-\frac{\cot\phi_2\sin\tau_{36}}{\sin\phi_{216}}(\sin\phi_{416}\sin\delta^5{}_{67}-\cos\phi_{216}\sin\phi_{214}\sin\delta^5{}_{27})S^{14}{}_{75}Q_{12}\right.$ $-\frac{\cot\phi_4\sin\tau_{57}}{\sin\phi_{417}}(\sin\phi_{217}\sin\delta^3{}_{76}-\cos\phi_{417}\sin\phi_{214}\sin\delta^3{}_{46})S^{12}{}_{63}Q_{14}$ $\left.+\cot\phi_2\cot\phi_4\sin\tau_{36}\sin\tau_{57}\left[\frac{\cos\phi_{214}(\cos\phi_{214}\cos\phi_{617}-\cos\phi_{416}\cos\phi_{217})}{\sin\phi_{216}\sin\phi_{417}}-\sin^2\phi_{214}\sin\delta^5{}_{27}\sin\delta^3{}_{46}\right]Q_{12}Q_{14}\right\}\mu_1$

dinates involved possess one or more atoms in common. In the subsequent tabulations this number of common atoms is indicated by the superscript p; writing the subscripts always in such an order that $\alpha\leq\alpha'$, where α = number of atoms in first coordinate, α' = number of atoms in second coordinate, it is clear that $1\leq p\leq\alpha$. In the present paper, only acyclic configurations of atoms defining the superposition of coordinates q and q' will be considered, i.e., the collection of atoms and bonds will be "trees" in the topological sense as defined by Cayley.[9] This being the case, it is possible to specify the distinct types of configurations uniquely through the following system of notation: imagine the set of common atoms to be drawn in a horizontal line, with the residual atoms of coordinate q drawn in lines with slopes of $\pm 45°$ upwards away from each end of the common set, and with the residual atoms of coordinate q' similarly drawn downwards (see Fig. 1). Then a two by two matrix, C, whose elements are the numbers of residual atoms in the corresponding corners of the pattern just described, would define the configuration precisely. However, only the first column of this

[9] A. Cayley, Phil. Mag. **13**, 172 (1857).

matrix need be given, since $C_{q1}+C_{q2}=\alpha-p$ and $C_{q'1}+C_{q'2}=\alpha'-p$. Furthermore, in computing the number of distinct configurations, the equivalence of the atoms in each coordinate by pairs beginning at the ends and progressing towards the center must be considered (corresponding to the permutation symbols in Eqs. (2) to (10)). For example, if q is a stretching coordinate (type r) and q' is a bending coordinate (type ϕ), and an interaction term with two common atoms is under consideration ($g^2{}_{r\phi}$), one could represent such an interaction by the matrices $\binom{00}{10}$ or $\binom{00}{01}$ which correspond, respectively, to cases in which the non-common atom of the ϕ coordinate is the first or third atom in the set defining ϕ, reading from left to right in the standard configuration diagram described above. Because of the equivalence of the **S** vectors for the two atoms of coordinate r and for the first and third atoms of coordinate ϕ, the two matrices represent equivalent interaction terms; in the tables, the first column of C is given where C is chosen in such a way that $C_{q1}\geq C_{q2}$, and if $C_{q1}=C_{q2}$, such that $C_{q'1}\geq C_{q'2}$. Explicit solutions of the combinatorial problem, giving the number, $n^p{}_{qq'}$ of distinct $g^p{}_{qq'}$, in terms of α, α', and p may be readily obtained, but the results are merely summarized in Table I. The columns headed by q, q', p, and $n^p{}_{qq'}$ need no further definition; the final column gives the first column of the matrix C for each distinct $g^p{}_{qq'}$ (i.e., the number of residual atoms of coordinate q above a similar number for coordinate q' at the left-hand end of the pattern).

Finally, it is necessary to establish a convention for numbering the atoms in each of the 33 possible configurations described above. The system followed throughout the tabulation of formulas given below in Section III is as follows: the numbering starts with the atoms common to both coordinates, reading from right to left along the horizontal line described above; the residual atoms are then numbered outwards from the set of common atoms, taking the upper left, lower left, upper right, and lower right corners of the diagram in that order. It is furthermore to be understood that C_{q1} and $C_{q'1}$ refer to the total number of residual atoms of each coordinate at the left-hand end of the diagram. This is illustrated in Fig. 1 for several configurations; examples of coordinates from well-known molecules are cited with each configuration diagram in the figure.

III. TABULATION OF FORMULAS

In the succeeding tables, it will be found that the algebraic expressions become rather cumbersome toward the end in the general case. While one purpose of the collection of formulas is to be as explicit as possible, some abbreviations are

TABLE III. Special formulas: all $\phi=90°$.

$g^2{}_{rr}$	$\mu_1+\mu_2$	$g^2{}_{\phi r}\binom{1}{2}$	$\pm Q^2{}_{12}(\mu_1+\mu_2)$ $[\pm\delta^5{}_{13}]$
$g^1{}_{rr}$	0	$\binom{1}{1}$	$-Q_{12}(\sin\tau_{35}Q_{15}\mu_1\pm Q_{24}\mu_2)$ $[\pm\delta^5{}_{34}]$
$g^2{}_{r\phi}$	$-Q_{23}\mu_2$	$\binom{1}{0}$	$\sin\tau_{34}Q^2{}_{12}(\mu_1+\mu_2)$
$g^1{}_{r\phi}\binom{1}{2}$	$\cos\tau Q_{13}\mu_1$	$g^1{}_{\phi r}\binom{2}{3}$	$-\cos\tau_{25}\sin\tau_{34}Q_{12}Q_{14}\mu_1$
$\binom{1}{1}$	0	$\binom{2}{2}$	0
$g^2{}_{rr}\binom{0}{2}$	0	$\binom{1}{3}$	$(\sin\tau_{64}Q_{12}+\sin\tau_{24}Q_{16})Q_{13}\mu_1$
$\binom{0}{1}$	0	$\binom{1}{2}$	——
$g^1{}_{rr}\binom{1}{3}$	$-\sin\tau_{24}Q_{13}\mu_1$	$g^4{}_{rr}$	$Q^2{}_{12}(\mu_1+\mu_2)+Q^2{}_{34}(\mu_3+\mu_4)$
$\binom{1}{2}$	$\pm Q_{15}\mu_1$ $[\pm\delta^4{}_{25}]$	$g^3{}_{rr}\binom{1}{1}$	$Q^2{}_{12}(\mu_1+\mu_2)$
$g^3{}_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3+(Q^2{}_{12}+Q^2{}_{23})\mu_2$	$\binom{1}{0}$	$-(\cos\tau_{35}Q_{15}Q_{12}\mu_1+\cos\tau_{14}Q_{34}Q_{32}\mu_3+Q_{12}Q_{32}\mu_2)$
$g^2{}_{\phi\phi}\binom{1}{1}$	$Q_{23}Q_{24}\mu_2$	$g^2{}_{rr}\binom{2}{2}$	0
$\binom{1}{0}$	$-\cos\tau Q^2{}_{12}(\mu_1+\mu_2)$	$\binom{2}{1}$	$-\cos\tau_{36}Q_{12}Q_{16}\mu_1$
$g^1{}_{\phi\phi}\binom{2}{2}$	$-\sin\tau_{25}\sin\tau_{34}Q_{12}Q_{14}\mu_1$	$\binom{2}{0}$	$\cos\tau_{35}Q^2{}_{12}(\mu_1+\mu_2)$
$\binom{2}{1}$	$-(\cos\tau_{35}Q_{14}+\cos\tau_{34}Q_{15})Q_{12}\mu_1$	$\binom{1}{1}$	0
$\binom{1}{1}$	——	$g^1{}_{rr}\binom{3}{3}$	$-\cos\tau_{35}\cos\tau_{26}Q_{12}Q_{15}\mu_1$
$g^3{}_{\phi r}$	$-\sin\tau Q_{23}Q_{34}\mu_3$	$\binom{3}{2}$	0
		$\binom{2}{2}$	——

TABLE IV. Special formulas: all $\phi = 109°28'$.

$g^2{}_{rr}$	$\mu_1+\mu_2$	$g^3{}_{\phi\tau}$	$-(2^{-\frac{1}{2}}/3)\sin\tau Q_{23}[(3Q_{23}+Q_{12})\mu_2+3(3Q_{34}+Q_{23})\mu_3]$
$g^1{}_{rr}$	$-\mu_1/3$	$g^2{}_{\phi\tau}(^1_2)$	$(2^{\frac{1}{2}}/24)\{\pm 3^{5/2}Q^2{}_{12}\mu_1+[\pm 3^{\frac{1}{2}}(3Q_{12}+Q_{23})[3Q_{12}+(1+\cos\tau_{15})Q_{24}]$
$g^2{}_{r\phi}$	$-(2)^{\frac{1}{2}}Q_{23}\mu_2/3$		$+\sin\tau_{15}Q_{24}(Q_{12}-5Q_{23})]\mu_2\}$ $[\pm\delta^5{}_{13}]$
$g^1{}_{r\phi}(^1_2)$	$(2)^{\frac{1}{2}}\cos\tau Q_{13}\mu_1/3$	$(^1_1)$	$-(2^{\frac{1}{2}}/24)[[18\sin\tau_{35}Q_{15}+(\pm 3^{\frac{1}{2}}+2\sin\tau_{35})Q_{12}]Q_{12}\mu_1$
$(^1_1)$	$(2)^{\frac{1}{2}}(Q_{13}+Q_{14})\mu_1/3$		$+(3Q_{12}+Q_{23})[\pm 3^{\frac{1}{2}}Q_{24}+(\pm 3^{\frac{1}{2}}+2\sin\tau_{35})Q_{12}]\mu_2]$ $[\pm\delta^5{}_{34}]$
$g^2{}_{\tau\tau}(^0_2)$	$\sin\tau Q_{23}\mu_2/3$	$(^1_0)$	$(2^{-\frac{1}{2}}/3)\{[9\sin\tau_{34}Q_{12}+[\sin\tau_{25}\cos\tau_{34}$
$(^0_1)$	0		$+3\sin\tau_{34}(1+\cos\tau_{25})]Q_{14}]\mu_1+3\sin\tau_{34}(3Q_{12}+Q_{23})\mu_2\}Q_{12}$
$g^1{}_{\tau\tau}(^1_3)$	$-\sin\tau_{24}Q_{13}\mu_1$	$g^1{}_{\phi\tau}(^2_3)$	$-(2)^{-\frac{1}{2}}(3\sin\tau_{34}\cos\tau_{25}+\cos\tau_{34}\sin\tau_{25})Q_{12}Q_{14}\mu_1$
$(^1_2)$	$[\pm 3^{\frac{1}{2}}Q_{15}+(2\sin\tau_{24}\pm 3^{\frac{1}{2}})Q_{13}]\mu_1/6$ $[\pm\delta^4{}_{25}]$	$(^2_2)$	$(2^{\frac{1}{2}}/36)Q_{12}[3(\sin\tau_{36}-\sin\tau_{34})[3Q_{16}+(1+\cos\tau_{56})Q_{12}]$ $+(\cos\tau_{36}-\cos\tau_{34}\pm 4\cdot 3^{\frac{1}{2}}\sin\tau_{34})\sin\tau_{56}Q_{14}]\mu_1$ $[\pm\delta^3{}_{46}]$
$g^3{}_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3+(3Q^2{}_{12}+3Q^2{}_{23}+2Q_{12}Q_{23})\mu_2/3$		
$g^2{}_{\phi\phi}(^1_1)$	$-(1/6)[3Q^2{}_{21}\mu_1+[3Q^2{}_{21}+(Q_{23}+Q_{24})Q_{21}-5Q_{23}Q_{24}]\mu_2]$		
$(^1_0)$	$-(1/3)\cos\tau Q_{12}[(3Q_{12}+Q_{14})\mu_1+(3Q_{12}+Q_{23})\mu_2]$		
$g^1{}_{\phi\phi}(^2_2)$	$-(1/3)(3\sin\tau_{25}\sin\tau_{34}-\cos\tau_{25}\cos\tau_{34})Q_{12}Q_{14}\mu_1$		
$(^2_1)$	$-(1/3)[(3\cos\tau_{35}+\cos\tau_{34})Q_{14}+(3\cos\tau_{34}+\cos\tau_{35})Q_{15}]Q_{12}\mu_1$		
$(^1_1)$	$-(2/3)(Q_{12}+Q_{14})(Q_{13}+Q_{15})\mu_1$		
$g^1{}_{\phi\tau}(^1_2)$	$(2)^{-\frac{1}{2}}[(3\sin\tau_{64}+\sin\tau_{24})Q_{12}+(3\sin\tau_{24}+\sin\tau_{64})Q_{16}]Q_{13}\mu_1$		
$(^1_2)$	$(2^{\frac{1}{2}}/24)[\pm 2\cdot 3^{\frac{1}{2}}(Q_{15}-Q_{12})Q_{16}+[(\pm 3^{\frac{1}{2}}-2\sin\tau_{24})(3Q_{15}+Q_{12})+(\mp 3^{\frac{1}{2}}-2\sin\tau_{54})(3Q_{12}+Q_{15})]Q_{13}]\mu_1$ $[\pm\delta^4{}_{25}]$		
$g^4{}_{\tau\tau}$	$(1/8)[9Q^2{}_{12}\mu_1+9Q^2{}_{34}\mu_4+[9Q^2{}_{12}+2(1+\cos\tau)Q^2{}_{23}+6(1+\cos\tau)Q_{12}Q_{23}]\mu_2$ $+[9Q^2{}_{34}+2(1+\cos\tau)Q^2{}_{23}+6(1+\cos\tau)Q_{34}Q_{23}]\mu_3]$		
$g^3{}_{\tau\tau}(^1_1)$	$(1/16)\{18Q^2{}_{12}\mu_1+[18Q^2{}_{12}+6(2+\cos\tau_{14}+\cos\tau_{15})Q_{12}Q_{23}+(1+2\cos\tau_{14}+2\cos\tau_{15})Q^2{}_{23}]\mu_2$ $+[(1+2\cos\tau_{14}+2\cos\tau_{15})Q^2{}_{23}+3Q_{23}[(2\cos\tau_{14}-1)Q_{34}+(2\cos\tau_{15}-1)Q_{35}]-9Q_{34}Q_{35}]\mu_3\}$		
$(^1_0)$	$-(1/24)\{9Q_{12}[(1+\cos\tau_{35})Q_{12}+3\cos\tau_{35}Q_{15}]\mu_1+9Q_{23}[(1+\cos\tau_{14})Q_{23}+3\cos\tau_{14}Q_{34}]\mu_3$ $+[3[3Q_{12}+(1+\cos\tau_{14})Q_{23}][3Q_{23}+(1+\cos\tau_{35})Q_{12}]-\sin\tau_{14}\sin\tau_{35}Q_{12}Q_{23}]\mu_2\}$		
$g^2{}_{\tau\tau}(^2_2)$	$-(1/96)\{54Q^2{}_{12}\mu_1+[54Q^2{}_{12}+3Q_{12}[(6(1+\cos\tau_{14})\mp 3^{\frac{1}{2}}\sin\tau_{14})Q_{23}+(6(1+\cos\tau_{16})\pm 3^{\frac{1}{2}}\sin\tau_{16})Q_{25}]$ $+[6(1+\cos\tau_{14})(1+\cos\tau_{16})-10\sin\tau_{14}\sin\tau_{16}\pm 3^{\frac{1}{2}}(\sin(\tau_{16}-\tau_{14})+\sin\tau_{16}-\sin\tau_{14})]Q_{23}Q_{25}]\mu_2\}$ $[\pm\delta^4{}_{15}]$		
$(^2_1)$	$-(1/48)\{[9(2\cos\tau_{63}-1)Q_{12}+54\cos\tau_{63}Q_{16}]Q_{12}\mu_1-[3[3Q_{12}+(1+\cos\tau_{14})Q_{23}][3Q_{25}+(1+\cos\tau_{56})Q_{12}]$ $\mp 3^{\frac{1}{2}}\sin\tau_{14}[3Q_{25}+(1+\cos\tau_{56})Q_{12}]Q_{23}\mp 3^{\frac{1}{2}}\sin\tau_{56}[3Q_{12}+(1+\cos\tau_{14})Q_{23}]Q_{12}-\sin\tau_{14}\sin\tau_{56}Q_{12}Q_{23}]\mu_2\}$ $[\pm\delta^6{}_{53}]$		
$(^2_0)$	$(1/8)Q_{12}\{[9\cos\tau_{35}Q_{12}+[3\cos\tau_{35}(1+\cos\tau_{26})-\sin\tau_{35}\sin\tau_{26}]Q_{15}]\mu_1$ $+[9\cos\tau_{35}Q_{12}+[3\cos\tau_{35}(1+\cos\tau_{14})-\sin\tau_{35}\sin\tau_{14}]Q_{23}]\mu_2\}$		
$(^1_1)$	$-(1/16)\{[[3Q_{15}+(1+\cos\tau_{53})Q_{12}][3Q_{16}+(1+\cos\tau_{64})Q_{12}]+\sin\tau_{53}\sin\tau_{64}Q^2{}_{12}$ $\pm 3^{\frac{1}{2}}\sin\tau_{64}Q_{12}[3Q_{15}+(1+\cos\tau_{53})Q_{12}]\mp 3^{\frac{1}{2}}\sin\tau_{53}Q_{12}[3Q_{16}+(1+\cos\tau_{64})Q_{12}]]\mu_1$ $[\pm\delta^3{}_{56}]$		
	$+[[3Q_{23}+(1+\cos\tau_{35})Q_{21}][3Q_{24}+(1+\cos\tau_{46})Q_{21}]+\sin\tau_{35}\sin\tau_{46}Q^2{}_{21}$ $\mp 3^{\frac{1}{2}}\sin\tau_{46}Q_{21}[3Q_{23}+(1+\cos\tau_{35})Q_{21}]\pm 3^{\frac{1}{2}}\sin\tau_{35}Q_{21}[3Q_{24}+(1+\cos\tau_{46})Q_{21}]]\mu_2$ $[\pm\delta^5{}_{34}]$		
$g^1{}_{\tau\tau}(^3_3)$	$-(3/8)(3\cos\tau_{35}\cos\tau_{26}+\sin\tau_{35}\sin\tau_{26})Q_{12}Q_{15}\mu_1$		
$(^3_2)$	$(1/16)[3^{\frac{1}{2}}(\pm\sin\tau_{35}-3^{\frac{1}{2}}\cos\tau_{35})Q_{17}+[3\cos\tau_{35}(2\cos\tau_{26}-1)+\sin\tau_{35}(\pm 3^{\frac{1}{2}}-2\sin\tau_{26})]Q_{15}]Q_{12}\mu_1$ $[\pm\delta^6{}_{72}]$		
$(^2_2)$	$(1/24)\{\pm 3^{\frac{1}{2}}[\sin\tau_{63}[3Q_{17}+(1+\cos\tau_{75})Q_{14}]Q_{12}+\sin\tau_{75}[3Q_{16}+(1+\cos\tau_{63})Q_{12}]Q_{14}]$ $-2\sin\tau_{63}\sin\tau_{75}Q_{12}Q_{14}\}\mu_1$ $[\pm\delta^5{}_{67}]$		

imperative. The following have been adopted:

$$\psi^i{}_{jkl}=\psi^i{}_{lkj}=\cos\phi_{jil}-\cos\phi_{jik}\cos\phi_{kil},$$

$$S^{ik}{}_{il}=(Q_{ij}/\sin\phi_{ijk})-(\cos\tau_{il}\cot\phi_{jkl}+\cot\phi_{ijk})Q_{jk},$$

and

$$\delta^k{}_{ij}=\tau_{ik}-\tau_{jk}.$$

The transformation properties of the several types of $g^p{}_{qq'}$ should be noted carefully. Under a reflection (generally an improper rotation), coordinates of the first two types are unchanged, whereas the third type, the twisting, suffers a change of sign.

Thus, the blocks of the G Matrix corresponding to elements of the types $g^p{}_{rr}$ and $g^p{}_{\phi\tau}$ for enantiomorphous configurations will be found to change sign. The eigenvalues are unaffected, of course,

since similar blocks in the F (potential energy) matrix also change sign.

Table II contains the general expressions (the symbol $\begin{pmatrix} C_{q1} \\ C_{q'1} \end{pmatrix}$ is omitted wherever $n^p{}_{qq'}=1$); in cases of extreme symmetry, it may occasionally be found preferable to develop the formulas by simplifying Eqs. (2) to (10) first and substituting in Eq. (1), using the table as a check. In cases practically devoid of symmetry, the general formulas serve both for direct calculation, and as a means of assessing ahead of time the magnitude of the numerical labor.

In addition to the general case, the appropriate expressions for the $g^p{}_{qq'}$ are given in Tables III, IV, and V for the cases in which all ϕ assume the special values of 90°, 109°28′ (tetrahedral angle), and 120°. In Tables III and IV, some of the formulas will be found to contain a choice of sign. The proper sign is readily determined by taking the upper sign throughout if a $\delta^k{}_{ij}$ enclosed in brackets after the formula in question is positive or the lower sign if $\delta^k{}_{ij}$ is negative (the sign of $\delta^k{}_{ij}$ follows the same convention as that for τ_{ij}). There is just one case, namely, $g^2{}_{\tau\tau}(^1_1)$ in Table IV, in which there occur two simultaneous choices of sign. As indicated in the table, upper signs are to be chosen for the coefficient of μ_1, if $\delta^3{}_{56}$ is positive, lower if $\delta^3{}_{56}$ is negative, whereas $\delta^5{}_{34}$ provides a similar criterion for the choice of signs in the coefficients of μ_2.

Finally, it should be noted that the formulas for $g^1{}_{\phi\phi}(^1_1)$, $g^1{}_{\phi\tau}(^1_2)$, and $g^1{}_{\tau\tau}(^2_2)$ are left blank in Tables III and V. This is because the associated configurations involve a tetravalent atom at which it is geometrically impossible to satisfy the condition that *all* bond angles be 90° or 120°.

TABLE V. Special formulas: all $\phi=120°$.

$g^2{}_{\tau\tau}$	$\mu_1+\mu_2$	$g^2{}_{\phi\phi}(^1_1)$	$-(1/2)[2Q^2{}_{12}\mu_1+[Q_{12}(2Q_{12}+Q_{23}+Q_{24})-Q_{23}Q_{24}]\mu_2]$
$g^1{}_{\tau\tau}$	$-\mu_1/2$	$(^1_0)$	$-(1/2)\cos\tau Q_{12}[(2Q_{12}+Q_{14})\mu_1+(2Q_{12}+Q_{23})\mu_2]$
$g^2{}_{\tau\phi}$	$-(3^1\!/_2)Q_{23}\mu_2$	$g^1{}_{\phi\phi}(^2_2)$	$(1/2)(\cos\tau_{25}\cos\tau_{34}-2\sin\tau_{25}\sin\tau_{34})Q_{12}Q_{14}\mu_1$
$g^1{}_{\tau\phi}(^1_2)$	$(3^1\!/_2)\cos\tau Q_{13}\mu_1$	$(^2_1)$	$(1/2)\cos\tau_{34}(Q_{15}-Q_{14})Q_{12}\mu_1$
$(^1_1)$	$(3^1\!/_2)(Q_{13}+Q_{14})\mu_1$	$(^1_1)$	——
$g^2{}_{\tau\tau}(^0_2)$	$(1/2)\sin\tau Q_{23}\mu_2$	$g^3{}_{\phi\tau}$	$-(3^1\!/_6)\sin\tau Q_{23}[(2Q_{23}+Q_{12})\mu_2+2(2Q_{34}+Q_{23})\mu_3]$
$(^0_1)$	0	$g^2{}_{\phi\tau}(^1_2)$	$(3^1\!/_6)\sin\tau_{15}(Q_{12}-Q_{23})Q_{24}\mu_2$
$g^1{}_{\tau\tau}(^1_3)$	$-\sin\tau_{24}Q_{13}\mu_1$	$(^1_1)$	$-(3^1\!/_6)\sin\tau_{35}Q_{12}[2(2Q_{15}+Q_{12})\mu_1+(2Q_{12}+Q_{23})\mu_2]$
$(^1_2)$	$(1/2)\sin\tau_{24}Q_{13}\mu_1$	$(^1_0)$	$(3^1\!/_6)Q_{12}\{[2\sin\tau_{34}[2Q_{12}+(1+\cos\tau_{25})Q_{14}]+\sin\tau_{25}\cos\tau_{34}Q_{14}]\mu_1$
$g^3{}_{\phi\phi}$	$Q^2{}_{12}\mu_1+Q^2{}_{23}\mu_3$		$+2\sin\tau_{34}(2Q_{12}+Q_{23})\mu_2\}$
	$+(Q^2{}_{12}+Q^2{}_{23}+Q_{12}Q_{23})\mu_2$	$g^1{}_{\phi\tau}(^2_3)$	$-(3^{-1}\!/_2)(\sin\tau_{25}\cos\tau_{34}+2\cos\tau_{25}\sin\tau_{34})Q_{12}Q_{14}\mu_1$
$g^1{}_{\phi\tau}(^2_2)$	$(3^1\!/_6)Q_{12}[4\sin\tau_{36}Q_{16}+[2(1+\cos\tau_{56})\sin\tau_{36}+\cos\tau_{36}\sin\tau_{56}]Q_{14}]\mu_1$		
$(^1_3)$	$(3^{-1}\!/_2)\sin\tau_{24}(Q_{16}-Q_{12})Q_{13}\mu_1$		
$(^1_2)$	——		
$g^4{}_{\tau\tau}$	$(2/3)[2Q^2{}_{12}\mu_1+2Q^2{}_{34}\mu_4+[2Q^2{}_{12}+(1+\cos\tau)Q^2{}_{23}+2(1+\cos\tau)Q_{12}Q_{23}]\mu_2$		
	$+[2Q^2{}_{34}+(1+\cos\tau)Q^2{}_{23}+2(1+\cos\tau)Q_{34}Q_{23}]\mu_3]$		
$g^3{}_{\tau\tau}(^1_1)$	$(2/3)\{2Q^2{}_{12}\mu_1+2Q_{12}(Q_{12}+Q_{23})\mu_2-[2Q_{34}Q_{35}+[(1+\cos\tau_{14})Q_{35}+(1-\cos\tau_{14})Q_{34}]Q_{23}]\mu_3\}$		
$(^1_0)$	$-(1/6)\{4[(1+\cos\tau_{35})Q_{12}+2\cos\tau_{35}Q_{15}]Q_{12}\mu_1+4[(1+\cos\tau_{14})Q_{32}+2\cos\tau_{14}Q_{34}]Q_{32}\mu_3$		
	$+[4[(1+\cos\tau_{35})Q^2{}_{12}+(1+\cos\tau_{14})Q^2{}_{23}]+[8+2(1+\cos\tau_{14})(1+\cos\tau_{35})-\sin\tau_{14}\sin\tau_{35}]Q_{12}Q_{32}]\mu_2\}$		
$g^2{}_{\tau\tau}(^2_2)$	$-(1/6)\{8Q^2{}_{12}\mu_1+[2[2Q_{12}+(1+\cos\tau_{14})Q_{23}][2Q_{12}+(1+\cos\tau_{16})Q_{25}]-\sin\tau_{14}\sin\tau_{16}Q_{23}Q_{25}]\mu_2\}$		
$(^2_1)$	$(1/6)\{4[(1-\cos\tau_{36})Q_{12}-2\cos\tau_{36}Q_{16}]Q_{12}\mu_1+[2[2Q_{12}+(1+\cos\tau_{14})Q_{23}][2Q_{25}+(1+\cos\tau_{56})Q_{12}]$		
	$-\sin\tau_{14}\sin\tau_{56}Q_{12}Q_{23}]\mu_2\}$		
$(^2_0)$	$(1/3)Q_{12}\{[2\cos\tau_{35}[2Q_{12}+(1+\cos\tau_{26})Q_{15}]-\sin\tau_{35}\sin\tau_{26}Q_{15}]\mu_1$		
	$+[2\cos\tau_{35}[2Q_{12}+(1+\cos\tau_{14})Q_{23}]-\sin\tau_{35}\sin\tau_{14}Q_{23}]\mu_2\}$		
$(^1_1)$	$-(2/3)[[2Q_{15}Q_{16}+(1+\cos\tau_{35})Q_{12}(Q_{12}+Q_{15}+Q_{16})]\mu_1+[2Q_{23}Q_{24}+(1+\cos\tau_{35})Q_{12}(Q_{12}+Q_{23}+Q_{24})]\mu_2]$		
$g^1{}_{\tau\tau}(^3_3)$	$-(2/3)(\sin\tau_{35}\sin\tau_{26}+2\cos\tau_{35}\cos\tau_{26})Q_{12}Q_{15}\mu_1$		
$(^3_2)$	$-(1/3)[4\cos\tau_{35}Q_{17}+[2\cos\tau_{35}(1-\cos\tau_{26})+\sin\tau_{35}\sin\tau_{26}]Q_{15}]Q_{12}\mu_1$		
$(^2_2)$	——		

IV. EXAMPLES OF APPLICATION TO SPECIFIC MOLECULES

1. H_2O_2 (C_2 Symmetry)

Choose as internal coordinates the O−O and O−H stretches (calling the coordinates P and R_i, respectively), the O−O−H bending (α_i), the H−O−O−H twisting (β); the index i on R and α identifies the H atom involved. Let $Q_{O-O}=P_0$, $Q_{O-H}=R_0$, $\phi_{O-O-H}=\alpha_0$, $\tau_{H-O-O-H}=\beta_0$. Then the following elements of the G matrix associated with the indicated coordinates may be found from Table II.

TABLE VI.

Coordinate pair	Type	Formula
PP	$g^2_{\tau\tau}$	$2\mu_o$
PR_i	$g^1_{\tau\tau}$	$\cos\alpha_0\mu_o$
$P\alpha_i$	$g^2_{\tau\phi}$	$-\sin\alpha_0 R_0\mu_o$
$P\beta$	$g^2_{\tau\tau}(^0_1)$	0
R_iR_i	$g^2_{\tau\tau}$	$\mu_o+\mu_H$
R_1R_2	——	0
$R_i\alpha_i$	$g^2_{\tau\phi}$	$-\sin\alpha_0 P_0\mu_o$
$R_1\alpha_2$	$g^1_{\tau\phi}(^1_2)$	$\sin\alpha_0\cos\beta_0 P_0\mu_o$
$R_i\beta$	$g^2_{\tau\tau}(^0_2)$	$-\cos\alpha_0\sin\beta_0 P_0\mu_0$
$\alpha_i\alpha_i$	$g^3_{\phi\phi}$	$R^2{}_0\mu_H+(2P^2{}_0+R^2{}_0-2\cos\alpha_0 P_0R_0)\mu_o$
$\alpha_1\alpha_2$	$g^2_{\phi\phi}(^1_0)$	$-2\cos\beta_0(P_0-\cos\alpha_0R_0)P_0\mu_o$
$\alpha_i\beta$	$g^3_{\phi\tau}$	$\frac{\sin\beta_0}{\sin\alpha_0}[2\cos\alpha_0P_0-(1+\cos^2\alpha_0)R_0]P_0\mu_o$
$\beta\beta$	$g^4_{\tau\tau}$	$\frac{2}{\sin^2\alpha_0}[R^2{}_0\mu_H+[R^2{}_0+2\cos\alpha_0(1+\cos\beta_0)\times(\cos\alpha_0P_0-R_0)P_0]\mu_o]$

Count of these coordinates reveals three redundancies which correspond to the vanishing sums of six bending coordinates at each carbon atom. The special notation for the elements of the G matrix is given below, only the first row from each set of symmetrically equivalent coordinates being required.

	P_1	P_2	R_{11}	R_{12}	R_{21}	R_{22}	S_1	S_2	T_1	T_2	α_{11}	α_{12}	α_{21}	α_{22}	β_1	β_2	γ
P_1	$g^1{}_P$	$g^2{}_P$	g_{PR}	g_{PR}	0	0	g_{PS}	0	g_{PT}	g_{PT}	$g_{P\alpha}$	$g_{P\alpha}$	0	0	$g_{P\beta}$	0	$g_{P\gamma}$
R_{11}			$g^1{}_R$	$g^2{}_R$	0	0	g_{RS}	0	0	0	$g^1{}_{R\alpha}$	$g^2{}_{R\alpha}$	0	0	$g_{R\beta}$	0	0
S_1							g_S	0	0	0	$g_{S\alpha}$	$g_{S\alpha}$	0	0	$g_{S\beta}$	0	0
T_1									$g^1{}_T$	$g^2{}_T$	0	0	0	0	0	0	$g_{T\gamma}$
α_{11}											$g^1{}_\alpha$	$g^2{}_\alpha$	0	0	$g_{\alpha\beta}$	0	0
β_1															g_β	0	0
γ																	g_γ

	δ_{11}	δ_{12}	δ_{21}	δ_{22}	ϵ_1	ϵ_2	ζ_{11}	ζ_{12}	ζ_{21}	ζ_{22}	η	τ_1	τ_2
P_1	$g^1{}_{P\delta}$	$g^1{}_{P\delta}$	$g^2{}_{P\delta}$	$g^2{}_{P\delta}$	$g^1{}_{P\epsilon}$	$g^2{}_{P\epsilon}$	$g^1{}_{P\zeta}$	$g^1{}_{P\zeta}$	$g^2{}_{P\zeta}$	$g^2{}_{P\zeta}$	$g_{P\eta}$	$g^1{}_{P\tau}$	$g^2{}_{P\tau}$
R_{11}	$g^1{}_{R\delta}$	$g^2{}_{R\delta}$	0	0	$g_{R\epsilon}$	0	$g^1{}_{R\zeta}$	$g^2{}_{R\zeta}$	0	0	$g_{R\eta}$	$g^1{}_{R\tau}$	$g^2{}_{R\tau}$
S_1	$g_{S\delta}$	$g_{S\delta}$	0	0	$g_{S\epsilon}$	0	$g_{S\zeta}$	$g_{S\zeta}$	0	0	$g_{S\eta}$	$g^1{}_{S\tau}$	$g^2{}_{S\tau}$
T_1	$g^1{}_{T\delta}$	$g^2{}_{T\delta}$	$g^1{}_{T\delta}$	$g^2{}_{T\delta}$	$g_{T\epsilon}$	$g_{T\epsilon}$	$g^1{}_{T\zeta}$	$g^2{}_{T\zeta}$	$g^1{}_{T\zeta}$	$g^2{}_{T\zeta}$	$g_{T\eta}$	$g_{T\tau}$	$-g_{T\tau}$
α_{11}	$g^1{}_{\alpha\delta}$	$g^2{}_{\alpha\delta}$	0	0	$g_{\alpha\epsilon}$	0	$g^1{}_{\alpha\zeta}$	$g^2{}_{\alpha\zeta}$	0	0	$g_{\alpha\eta}$	$g^1{}_{\alpha\tau}$	$g^2{}_{\alpha\tau}$
β_1	$g_{\beta\delta}$	$g_{\beta\delta}$	0	0	$g_{\beta\epsilon}$	0	$g_{\beta\zeta}$	$g_{\beta\zeta}$	0	0	$g_{\beta\eta}$	$g^1{}_{\beta\tau}$	$g^2{}_{\beta\tau}$
γ	$g_{\gamma\delta}$	$g_{\gamma\delta}$	$g_{\gamma\delta}$	$g_{\gamma\delta}$	$g_{\gamma\epsilon}$	$g_{\gamma\epsilon}$	$g_{\gamma\zeta}$	$g_{\gamma\zeta}$	$g_{\gamma\zeta}$	$g_{\gamma\zeta}$	$g_{\gamma\eta}$	$g_{\gamma\tau}$	$g_{\gamma\tau}$
δ_{11}	$g^1{}_\delta$	$g^2{}_\delta$	$g^3{}_\delta$	$g^4{}_\delta$	$g^1{}_{\delta\epsilon}$	$g^2{}_{\delta\epsilon}$	$g^1{}_{\delta\zeta}$	$g^2{}_{\delta\zeta}$	$g^3{}_{\delta\zeta}$	$g^4{}_{\delta\zeta}$	$g_{\delta\eta}$	$g^1{}_{\delta\tau}$	$g^2{}_{\delta\tau}$
ϵ_1					$g^1{}_\epsilon$	$g^2{}_\epsilon$	$g^1{}_{\epsilon\zeta}$	$g^1{}_{\epsilon\zeta}$	$g^2{}_{\epsilon\zeta}$	$g^2{}_{\epsilon\zeta}$	$g_{\epsilon\eta}$	$g^1{}_{\epsilon\tau}$	$g^2{}_{\epsilon\tau}$
ζ_{11}							$g^1{}_\zeta$	$g^2{}_\zeta$	$g^3{}_\zeta$	$g^4{}_\zeta$	$g_{\zeta\eta}$	$g^1{}_{\zeta\tau}$	$g^2{}_{\zeta\tau}$
η											g_η	$g_{\eta\tau}$	$g_{\eta\tau}$
τ_1												$g^1{}_\tau$	$g^2{}_\tau$

2. C_3H_8 (Propane; C_{2v} Symmetry)

Assume tetrahedral valence angles throughout; consider one H on each methyl group and the three C to be coplanar and of the form indicated in Fig. 2. Then all τ are either $\pm60°$ or 180°. With atoms numbered as indicated in Fig. 2, choose the following coordinates:

TABLE VII.

Type	Symbol	Number	Detailed description
Stretching	P_i	2	C_3-C_i
Stretching	R_{ij}	4	C_i-H_{ij}
Stretching	S_i	2	C_i-H_{i3}
Stretching	T_i	2	C_3-H_{3i}
Bending	α_{ij}	4	$H_{ij}-C_i-H_{i3}$
Bending	β_i	2	$H_{i1}-C_i-H_{i2}$
Bending	γ	1	$H_{31}-C_3-H_{32}$
Bending	δ_{ij}	4	$H_{ij}-C_i-C_3$
Bending	ϵ_i	2	$H_{i3}-C_i-C_3$
Bending	ζ_{ij}	4	$H_{3j}-C_3-C_i$
Bending	η	1	$C_1-C_2-C_3$
Twisting	τ_i	2	$H_{i3}-C_i-C_3-C_{i\pm}$

The zeros in this matrix arise simply because the pairs of coordinates in question possess no common atoms. The matrix elements $g^1{}_{P\tau}$, $g^2{}_{P\tau}$, $g^1{}_{S\tau}$, $g^2{}_{S\tau}$, $g^1{}_{\beta\tau}$, $g^2{}_{\beta\tau}$, $g_{\gamma\tau}$, $g^1{}_{\epsilon\tau}$, $g^2{}_{\epsilon\tau}$, $g_{\eta\tau}$ also vanish without detailed calculation, since they represent interactions of one of the first two types of coordinates with the third type and the configurations of atoms defining them contain a plane of symmetry ($g^1{}_{P\tau}$ would vanish even without symmetry, being of type $g^2{}_{\tau\tau}(^0_1)$). Many of the remaining elements are equal: formulas for them are obtained by substitution of appropriate values for τ in Table IV. It is assumed that all C−H distances are equal; the reciprocal of such a distance is designated by R_0 and that of the C−C distance by P_0. Certain elements, fol-

TABLE VIII.

Type	G elements in $CH_3CH_2CH_3$	Formula
$g^2{}_{\tau\tau}$	$g^1{}_P$	$2\mu_C$
	$g^1{}_R=g^1{}_S=g^1{}_T$	$\mu_C+\mu_H$
$g^1{}_{\tau\tau}$	$g^2{}_P=g_{PR}=g_{PS}=g_{PT}=g^2{}_R=g_{RS}=g^2{}_T$	$-\mu_C/3$
$g^2{}_{\tau\phi}$	$g^1{}_{P\delta}=g^1{}_{P\epsilon}=g^1{}_{P\zeta}=g^1{}_{R\alpha}=g_{R\beta}=g_{S\alpha}=g_{T\gamma}$	$-(2\frac{1}{2}/3)R_0\mu_C$
	$g_{P\eta}=g^1{}_{R\delta}=g_{S\epsilon}=g^1{}_{T\zeta}$	$-(2\frac{1}{2}/3)$—$P_0\mu_C$
$g^1{}_{\tau\phi}(^1_2)$	$g^2{}_{P\delta}=g^1{}_{R\zeta}=g_{R\eta}=g_{S\zeta}=g^1{}_{T\delta}=g_{T\epsilon}$	$(2\frac{1}{2}/3)P_0\mu_C$
	$g^2{}_{P\epsilon}=g^2{}_{R\zeta}=g_{S\eta}=g^2{}_{T\delta}$	$-(2\frac{1}{2}/3)P_0\mu_C$
$(^1_1)$	$g_{P\alpha}=g_{P\beta}=g_{P\gamma}=g^2{}_{R\alpha}=g_{S\beta}$	$(2\frac{1}{2}/3)R_0\mu_C$
	$g^2{}_{P\zeta}=g^2{}_{R\delta}=g_{R\epsilon}=g_{S\delta}=g^2{}_{T\zeta}$	$(2\frac{1}{2}/3)(P_0+R_0)\mu_C$
	$g_{T\eta}$	$(2\frac{1}{2}/3)P_0\mu_C$
$g^1{}_{\tau\tau}(^1_0)$	$g^2{}_{R\tau}(\pm)$	$-(3\frac{1}{2})P_0\mu_C$
$(^1_2)$	$g^1{}_{R\tau}(\pm)=g_{T\tau}(\pm)$	$-(3\frac{1}{2})R_0\mu_C$
$g^3{}_{\phi\phi}$	$g^1{}_\alpha=g_\beta=g_\gamma$	$(2/3)R^2{}_0(3\mu_H+4\mu_C)$
	$g^1{}_\delta=g^1{}_\epsilon=g^1{}_\zeta$	$R_0{}^2\mu_H+(3R^2{}_0+6P^2{}_0+2R_0P_0)\mu_C/3$
	g_η	$(14/3)P^2{}_0\mu_C$
$g^2{}_{\phi\phi}(^1_1)$	$g^2{}_\alpha=g_{\alpha\beta}$	$-(1/2)R^2{}_0\mu_H$
	$g^2{}_\delta=g^1{}_{\delta\epsilon}=g^2{}_\zeta$	$-(1/6)(6P^2{}_0-5R^2{}_0+2P_0R_0)\mu_C$
	$g^3{}_\zeta$	$-(1/6)[3R^2{}_0\mu_H+(3R_0+5P_0)(R_0-P_0)\mu_C]$
	$g^1{}_{\alpha\delta}=g_{\alpha\epsilon}=g_{\beta\delta}=g_{\gamma\eta}$	$-(1/6)[3R^2{}_0\mu_H+4R_0(R_0-P_0)\mu_C]$
	$g_{\zeta\eta}$	$-(1/6)(7P_0-4R_0)P_0\mu_C$
$(^1_0)$	$g^2{}_{\delta\zeta}$	$(2/3)(3P_0+R_0)P_0\mu_C$
	$g_{\epsilon\eta}$	$(1/3)(7P_0+R_0)P_0\mu_C$
	$g^1{}_{\delta\zeta}=g^1{}_{\epsilon\zeta}$	$-(1/3)(3P_0+R_0)P_0\mu_C$
	$g_{\delta\eta}$	$-(1/6)(7P_0+R_0)P_0\mu_C$
$g^1{}_{\phi\phi}(^2_2)$	$g^2{}_\epsilon$	$(1/3)P^2{}_0\mu_C$
	$g^3{}_\delta$	$(5/6)P^2{}_0\mu_C$
	$g^4{}_\delta$	$-(2/3)P^2{}_0\mu_C$
	$g^2{}_{\delta\epsilon}$	$-(1/6)P^2{}_0\mu_C$
$(^2_1)$	$g^1{}_{\alpha\zeta}=g_{\beta\eta}=g_{\gamma\epsilon}$	$(4/3)P_0R_0\mu_C$
	$g^2{}_{\alpha\zeta}=g_{\alpha\eta}=g_{\beta\zeta}=g_{\gamma\delta}$	$-(2/3)P_0R_0\mu_C$
	$g^3{}_{\delta\zeta}$	$(2/3)(P_0+R_0)P_0\mu_C$
	$g^4{}_{\delta\zeta}$	$(1/6)(R_0-5P_0)P_0\mu_C$
	$g^2{}_{\epsilon\zeta}$	$(1/6)(P_0-5R_0)P_0\mu_C$
$(^1_1)$	$g_{\gamma\eta}$	$-(8/3)P_0R_0\mu_C$
	$g^4{}_\zeta$	$-(2/3)(P_0+R_0)^2\mu_C$
	$g^2{}_{\alpha\delta}=g_{\beta\epsilon}$	$-(4/3)(P_0+R_0)R_0\mu_C$
$g^2{}_{\phi\tau}(^1_2)$	$g^1{}_{\alpha\tau}(\pm)$	$(6\frac{1}{2}/8)R^2{}_0(3\mu_H+4\mu_C)$
	$g^2{}_{\zeta\tau}(\pm)$	$-(6\frac{1}{2}/8)(6P_0+R_0)P_0\mu_C$
$(^1_1)$	$g^1{}_{\delta\tau}(\pm)$	$(6\frac{1}{2}/8)R^2{}_0\mu_C$
	$g^1{}_{\zeta\tau}(\pm)$	$(6\frac{1}{2}/8)(3P_0-2R_0)P_0\mu_C$
$(^1_0)$	$g^2{}_{\delta\tau}(\pm)$	$6\frac{1}{2}(6P_0+R_0)P_0\mu_C$
$g^1{}_{\phi\tau}(^1_3)$	$g^2{}_{\alpha\tau}(\pm)$	$(6\frac{1}{2})P_0R_0\mu_C$
$g^4{}_{\tau\tau}$	$g^1{}_\tau$	$(9/8)[R^2{}_0\mu_H+(2P^2{}_0+R^2{}_0)\mu_C]$
$g^3{}_{\tau\tau}(^1_0)$	$g^2{}_\tau$	$(9/8)(2R_0-P_0)P_0\mu_C$

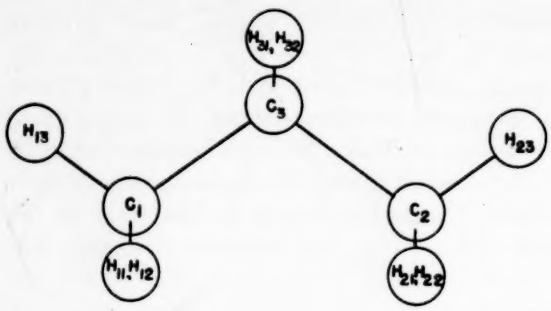


FIG. 2. Numbering of atoms in C_3H_8.

lowed by a $(\pm)$, would exhibit alternation of sign if the complete G matrix, rather than just the first row from each symmetrically equivalent set had been written out.

V. CONCLUSIONS

A few remarks on the limits of applicability of these formulas are necessary. In the first place, it remains to be seen whether the torsional type of coordinate introduced here will prove to be practical in the treatment of restricted rotation as a small vibration. This is not only a question of the magnitude of the potential barrier hindering the rotation and the quality of the harmonic approximation in the trough of the potential energy *versus* angle of torsion, but also of whether or not the vibrational potential function is reasonably diagonal in terms of this type of force constant. It should be mentioned at this point that such torsional frequencies as are known at present are usually known or inferred to be quite low by comparison with the bending and stretching frequencies, at least in the case of hydrocarbons. Taylor and Pitzer[10] have shown that an approximate treatment of such cases may advantageously be carried through in terms of the kinetic energy matrix (not its inverse).

From a purely kinematical point of view, the set of coordinates chosen here is inadequate for the treatment of such planar molecules as BF_3 or CH_2O which possess no chain of bonded atoms with a length of four atoms; when a structure similar to that of such molecules forms a part of a larger molecule, the same coordinate deficiency will remain. Another type of deficiency of the tables occurs when a part of the molecule contains a chain of 3 or more colinear atoms, since one or more dihedral angles become indeterminate. On the other hand, a large number of the G matrix elements for many cyclic molecules may be found in the tables, including, for example, all necessary in-plane interaction elements for benzene.

[10] W. J. Taylor and K. S. Pitzer, J. Research Nat. Bur. Stand. **38**, 1 (1947).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

The Vapor Pressures of Some Alkali Halides*

GERALDINE E. COGIN** AND GEORGE E. KIMBALL
Department of Chemistry, Columbia University, New York, New York

(Received April 21, 1948)

The vapor pressures of six alkali halides, NaBr, NaI, KI, CsCl, CsBr, and CsI, have been measured in the range from about 10^{-4}-mm to 0.1-mm pressure. The measurements were made by the diffusion method, using an oxygen-coated tungsten filament as detector.

I. INTRODUCTION

VAPOR pressures of solid alkali halides have been measured by a number of investigators. Mayer and Wintner[1] used Knudsen's method of molecular effusion.[2] The amount of salt Q escaping into a vacuum from an oven at temperature T through a small hole of known area A in a definite time interval t is related to the pressure P in the oven by

$$P=(Q/At)(2\pi RT/M)^{\frac{1}{2}},$$

where M is the molecular weight of the salt and R is the gas constant. The effused salt was condensed on a cold surface and the amount determined by quantitative chemical analysis. Niwa[3] and Dietz[4] used the same method, but measured the loss of weight of the oven. Dietz also used an electromagnetic balance as an absolute manometer.

Zimm and Mayer[5] combined Knudsen's effusion method with the positive ion method of Langmuir.[6] The effusing salt beam was intercepted by a tungsten filament whose temperature and work function were sufficiently high to allow complete dissociation of the salt molecule and complete ionization of the metal atom, and the current due to the metal ions was measured. This method gives directly the rate of effusion and thus eliminates the measurement of the time interval. It is not necessary to hold the oven temperature constant for long periods of time. The sensitivity of the detector allows the vapor pressure measurements to be extended to lower temperatures.

In this research, the method of Zimm and Mayer was used to measure the vapor pressures of sodium bromide, sodium iodide, potassium iodide, cesium chloride, cesium bromide, and cesium iodide. The heats and entropies of vaporization were calculated from these data. The entropies of the crystals at 800°K and the heats of vaporization at absolute zero were also calculated.

II. PRINCIPLES OF THE METHOD

The number of salt molecules escaping per second into a vacuum from an oven at known temperature through a hole whose diameter is smaller than the mean free path of the molecules is given by Knudsen's formula

$$n=SP/(2\pi mkT)^{\frac{1}{2}}, \qquad (1)$$

where S=area of hole, P=pressure inside oven, T=absolute temperature of oven, m=mass of molecules, and k=Boltzmann constant. The molecules leaving the oven are allowed to impinge upon a filament whose temperature and work function are sufficiently high so that every molecule hitting it is dissociated and every metal atom thus formed is ionized. If sufficient potential is put on the collector, the number of positive ions reaching it will equal the number of molecules hitting the filament. Consideration of the geometry of the apparatus allows the pressure in the oven to be expressed in terms of the positive ion current i_0.

$$P=[N_0R^2(2\pi mkT)^{\frac{1}{2}}/r^2AF]i_0, \qquad (2)$$

where r=radius of hole in oven, R=distance

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

** Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Columbia University.

[1] J. E. Mayer and I. H. Wintner, J. Chem. Phys. **6**, 301 (1938).

[2] M. Knudsen, Ann. d. Physik **47**, 697 (1915).

[3] K. Niwa, J. Faculty Sci. Hokkaido Imp. Univ. Ser. III, **2**, 201 (1938).

[4] V. Dietz, J. Chem. Phys. **4**, 575 (1936).

[5] B. H. Zimm and J. E. Mayer, J. Chem. Phys. **12**, 362 (1944).

[6] J. B. Taylor and I. Langmuir, Phys. Rev. **51**, 753 (1937).

between hole and filament, N_0=Avogadro's number, F=Faraday, and A=area of plane projection of filament.

The molecular effusion method allows the calculation of the vapor pressure from the effusion rate, provided the molecular weight of the gas is known. Zimm and Mayer showed it to be unlikely that the degree of association of KCl is greater than 0.3 percent at 800°K. Because the properties of the other alkali halide vapors are similar, it is assumed that the amount of dimerization is negligible in all cases. The extent of dissociation of the molecules into atoms may be estimated from the dissociation energy of the molecule. In the case of CsI, which has the lowest dissociation energy of the alkali halides, the dissociation would be about 5×10^{-5} percent at the vapor pressure of 10^{-2} mm at 800°K.

The pressure of positive ions produced by the dissociation of the gas in the oven to ions is even less than the dissociation into atoms, and is consequently negligible. In the case of CsI, the extent of dissociation is about 5×10^{-8} percent and corresponds to a pressure of cesium ions of 5×10^{-12} mm at 800°K. Even considering that the ions leaving the oven orifice carrying a current directly to the large collecting plate without requiring collision with the filament so that the geometric factor of R^2/A in Eq. (2) is much larger in this case, the low pressure negates any appreciable errors due to this cause.

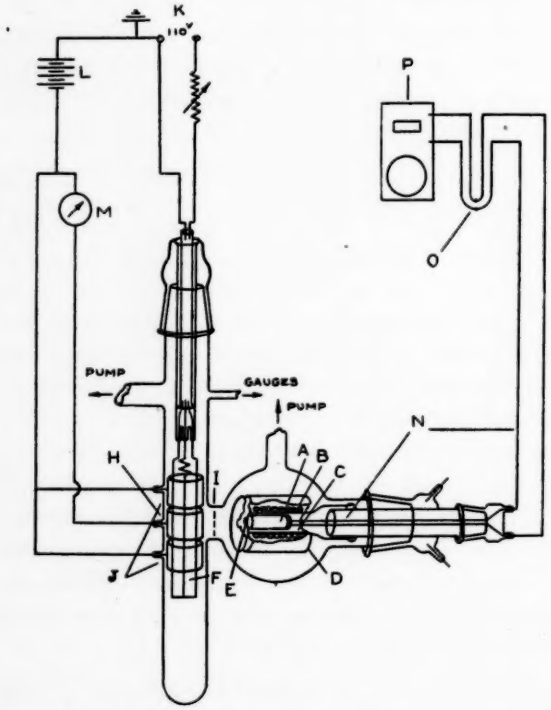


FIG. 1. Schematic diagram of the apparatus.

III. APPARATUS

A diagram of the apparatus is shown in Fig. 1. The oven A in which the salt was heated was a 4×1.5-cm polished silver cylinder whose wall thickness was 0.3 cm; the cover was 0.7 cm thick and screwed into the body of the oven to a depth of 0.4 cm. The hole E through which the molecules escaped was 0.1057 cm in diameter, finished with knife-sharp edges. Another oven, used for additional runs on cesium bromide, had a hole 0.0105 cm in diameter. The oven was heated by a Nichrome coil B wound around a quartz tube C; both were enclosed by a silver housing D. Current for heating the coil was taken from a Solar regulating transformer. The silver-constantan thermocouple N, used to measure the temperature of the oven, was inserted into a hole bored in a silver plug which was then flattened to hold the couple securely; the plug screwed deep into the cover of the oven. The cold junction O was kept in a bath of crushed ice and water; the e.m.f. of the couple was measured with a Leeds and Northrup Type K potentiometer P. The couple was standardized at the freezing point of Bureau of Standards samples of tin, zinc, and aluminum; when it was later checked at a single point, it showed no appreciable deviation from the initial calibration. The beam of escaping salt molecules, defined by the aperture in the collector plate H, fell on a tungsten filament F, 0.02 cm in diameter, which had been previously aged for one hour at 2600°K. The filament (13.5–14 cm long) was suspended vertically, using a heavy tungsten spring to keep it taut when heated. The length of the filament exposed to the molecules was approximately 2 cm. Current for heating the filament was supplied by the d.c. line K. The voltage drop across the filament could be measured by means of platinum potential leads welded to its ends. The diameter of the filament was initially determined by weigh-

TABLE I. Values of $(e\varphi - I)$ for $r = 99$.

Temperature °K	$(e\varphi - I)$ ev
1200	0.547
1400	0.638
1600	0.729
1800	0.820

TABLE II. Ionization potentials of the alkali metals.

Metal	Ionization potential ev
Sodium	5.138
Potassium	4.340
Cesium	3.893

ing a known length of aged wire. The diameter and temperature of the filament during the run were calculated from the tables of Jones and Langmuir.[7] The distance between the hole in the oven and the filament was approximately 10.50 cm. It was redetermined whenever changes were made in the tube elements. The ions leaving the filament were collected by the collector plate H; stray ions were collected by the guard ring J. The plates were attached to the same potential source L but connection from the collector was through a Leeds and Northrup Type HS galvanometer M whose sensitivity was 2.3×10^{-10} amp./mm. The beam leaving the oven could be interrupted by a magnetically operated shutter I.

Thermocouple wires were introduced into the apparatus through capillary tubes sealed with Apiezon wax "W;" all other wires were introduced by means of tungsten to glass seals. The plates were made of hydrogen fired "A" nickel. Two auxiliary filaments for outgassing were of tungsten. The filament and oven assemblies were introduced into the glass envelope by means of ground glass joints sealed with Apiezon "W." All stopcocks were greased with Apiezon "N."

The system was evacuated by two single-stage mercury diffusion pumps in parallel, with mechanical backing. Mercury vapor was eliminated by use of dry ice traps. Residual gas pressure was measured with a Distillation Products VG1A ionization gauge which had been calibrated against a McLeod gauge with liquid nitrogen traps.

[7] H. A. Jones and I. Langmuir, Gen. Elec. Rev. 310 (1937).

TABLE III. Dissociation energies of the alkali halide molecules.

Salt	Dissociation energy ev
NaBr	3.85
NaI	3.16
KI	3.33
CsCl	4.38
CsBr	3.99
CsI	3.32

TABLE IV. Experimental conditions and necessary values of work function to satisfy $r = 99$, $q = 99$.

Salt	Filament temp. T_f (°K)	$e\varphi$ for $r=99$ at T_f $(e\varphi)_{r=99}$ ev	Max. value N_{MX} $N\times10^{-14}$	Log K for $q=99$ at T_f	$e\varphi$ for $q=99$ at T_f $(e\varphi)_{q=99}$ ev
NaBr	1400	5.78	0.447	−4.76	5.69
NaI	1250	5.71	4.61	−3.69	5.64
KI	1600	5.07	2.71	−3.78	4.29
CsCl	1800	4.71	2.92	−3.73	4.41
CsBr	1400	4.53	1.07	−4.10	4.83
CsBr	1800	4.71	1.07	−4.05	3.96
CsI	1400	4.53	4.92	−3.48	4.38

IV. OPERATING CONDITIONS

A. Scattering

The relationship

$$P = [N_0 R^2 \cdot (2\pi mkT)^{\frac{1}{2}}/r^2 AF]i_0 \qquad (2)$$

has been derived assuming there is no scattering of the salt beam. If the molecules are moving a distance R with uniform velocity through a scattering gas, the number I of beam molecules received per second by a detector will be

$$I = I_0 e^{-R/L},$$

where I_0 is the number of beam molecules received per second by the detector in the absence of scattering gas and L the mean free path. The calculation of L will be uncertain because the scattering cross sections are unknown. Therefore, the scattering correction I/I_0 has been evaluated experimentally by measuring the positive ion current as a function of residual gas pressure (at constant oven and filament temperature) and extrapolating to zero pressure. The value of i_0 used in Eq. (2) was calculated from the observed positive ion current i by applying the scattering correction I/I_0. The pressure of residual gas was usually kept low enough so that I/I_0 was greater than 0.85. Within the working range, the curves of I/I_0 *versus* pressure

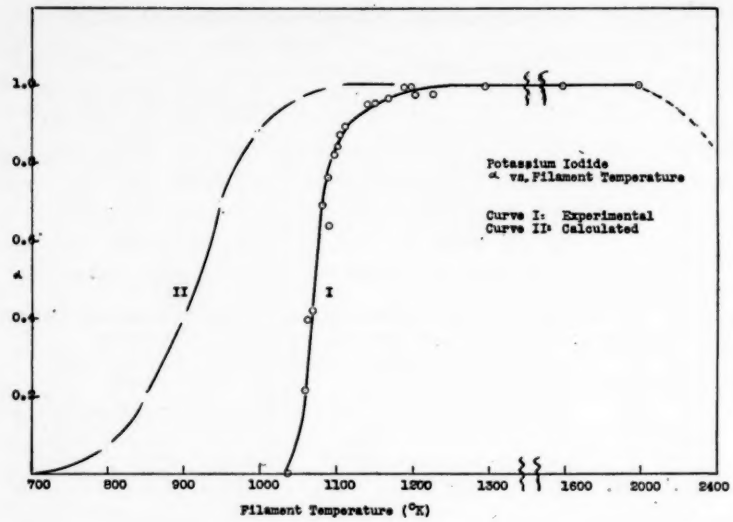


FIG. 2. Ion emission *versus* temperature.

for all the salts studied were within 5 percent of an average curve, and were reproducible within a few percent.

B. Reaction on the Filament

We will now consider the reaction

$$MX \rightarrow M^+ + X + e \text{ (in filament)} \qquad (I)$$

which occurs on the surface of the filament to determine whether the assumption of complete conversion of MX molecules to M^+ ions made in the derivation of Eq. (2) is valid.

1. Equilibrium of Conversion Reaction

The M atoms of the incoming MX molecules may leave the filament as MX molecules, M atoms, and M^+ ions only. The necessary conditions for complete conversion of MX to M^+ are that the equilibrium ratios

$$n_{M^+}/n_M \quad \text{and} \quad n_{M^+}/n_{MX}$$

are both extremely large. The two together are a sufficient condition, assuming no kinetic obstacle to the establishment of equilibrium. These ratios are given by

$$r = n_{M^+}/n_M = \tfrac{1}{2} \exp(e\varphi - I)/RT, \qquad (3)$$

where I = ionization potential of the atom and $e\varphi$ = work function of the filament surface. This is the Saha-Langmuir equation[8] assuming zero reflection coefficients for both atoms and ions. From the equilibrium constant of reaction (I) and the principle of conservation of matter one obtains:

$$q = n_{M^+}/n_{MX} = [K/n_{M^+}][r/(1+r)] \times [(1/2\pi\mu kT)^{\frac{1}{2}}], \qquad (4')$$

where K = equilibrium constant for reaction (I), $K = \exp[(e\varphi - D - I)/RT + (S_{M^+}° + S_X° + S_{MX}°)/R - \frac{1}{2}]$, and μ = reduced mass of MX. If the extent of reaction is so great that $n_{M^+} \gg n_{MX}$, then the number of M^+ ions leaving a unit area of filament per second, n_{M^+}, approximately equals the number of MX molecules striking a unit area of filament per second, N_{MX}.

$$q \doteq [K/N_{MX}][r/(1+r)][(1/2\pi\mu kT)^{\frac{1}{2}}]. \qquad (4)$$

A necessary and sufficient condition for 99 percent conversion of MX to M^+ is that both $r \geq 99$ and $q \geq 99$.

Table I lists the quantity $(e\varphi - I)$ which satisfies the relation $r = 99$ at various temperatures. It can be seen that the work function necessary to ionize 99 percent of the metal atoms increases with increasing temperature.

At a given pressure of salt molecules at the filament, the ratio q depends on the equilibrium constant for the over-all reaction K, which is a function of the ionization potential of the metal atom I, dissociation energy of the salt molecule D, work function of the filament $e\varphi$, temperature T, and the standard state entropy change $\Delta S°$. For any molecule D and I are fixed and $\Delta S°$

[8] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **107A**, 61 (1925).

TABLE V. Experimental data.

Sodium bromide		Sodium iodide	
$-\log p_{mm}$	$(1000/T)$ (°K)	$-\log p_{mm}$	$(1000/T)$ (°K)
1.77	1.098	0.49	1.108
1.91	1.114	1.11	1.160
2.05	1.129	1.20	1.169
2.32	1.153	1.49	1.190
2.62	1.179	1.83	1.221
2.67	1.182	2.03	1.244
2.82	1.197	2.13	1.253
2.87	1.201	2.17	1.255
3.15	1.228	2.67	1.300
3.73	1.278	2.75	1.311
3.98	1.301	3.27	1.358
4.20	1.319		
Potassium iodide		**Cesium chloride**	
$-\log p_{mm}$	$(1000/T)$ (°K)	$-\log p_{mm}$	$(1000/T)$ (°K)
0.90	1.114	0.89	1.122
1.24	1.144	1.12	1.141
1.37	1.152	1.16	1.146
1.39	1.153	1.58	1.184
1.46	1.162	1.60	1.185
1.63	1.177	1.73	1.200
1.67	1.179	1.85	1.209
1.69	1.179	2.03	1.223
1.95	1.207	2.37	1.256
1.98	1.209	2.40	1.263
2.00	1.204	2.61	1.281
2.00	1.209	2.71	1.290
2.02	1.205	2.78	1.298
2.29	1.237	2.80	1.305
2.43	1.251	3.01	1.321
2.51	1.260	3.05	1.325
2.56	1.263	3.17	1.336
2.63	1.262	3.33	1.354
2.63	1.264	3.43	1.363
2.93	1.301	3.55	1.379
2.94	1.297	3.58	1.381
2.94	1.302	3.76	1.397
2.95	1.297	3.85	1.406
3.09	1.315	3.88	1.409
3.44	1.344	3.88	1.413
3.51	1.356	4.02	1.421
3.55	1.363	4.14	1.435
3.81	1.383	4.25	1.449
3.84	1.386		
Cesium bromide			
$-\log p_{mm}$	$(1000/T)$ (°K)	$-\log p_{mm}$	$(1000/T)$ (°K)
0.92	1.111	1.92	1.202
1.00	1.120	1.95	1.210
1.02	1.121	1.95	1.210
1.21	1.141	1.97	1.215
1.21	1.141	2.00	1.209
1.22	1.145	2.00	1.218
1.23	1.145	2.04	1.220
1.24	1.144	2.13	1.230
1.24	1.146	2.23	1.236
1.26	1.144	2.25	1.237
1.26	1.148	2.25	1.239
1.27	1.153	2.37	1.243
1.31	1.150	2.38	1.254
1.38	1.158	2.39	1.255
1.39	1.161	2.42	1.266
1.40	1.159	2.48	1.255
1.40	1.159	2.50	1.261
1.44	1.162	2.55	1.271
1.44	1.165	2.66	1.277
1.47	1.164	2.69	1.277
1.49	1.166	2.69	1.281
1.49	1.168	2.70	1.281
1.49	1.170	2.84	1.291

TABLE V.—*Continued.*

Cesium iodide			
$-\log p_{mm}$	$(1000/T)$ (°K)	$-\log p_{mm}$	$(1000/T)$ (°K)
1.50	1.172	2.85	1.295
1.53	1.173	2.85	1.297
1.59	1.179	2.85	1.307
1.61	1.177	2.87	1.296
1.63	1.179	2.97	1.305
1.65	1.183	3.01	1.306
1.66	1.182	3.04	1.323
1.71	1.186	3.07	1.321
1.78	1.197	3.07	1.323
1.88	1.203	3.08	1.323
1.88	1.209	3.13	1.320
1.89	1.206	3.24	1.339
		3.41	1.353
0.59	1.118	2.07	1.253
0.62	1.120	2.07	1.254
0.70	1.128	2.27	1.265
0.71	1.127	2.32	1.273
0.96	1.147	2.58	1.305
0.99	1.151	2.63	1.310
1.32	1.182	2.73	1.315
1.35	1.179	2.85	1.327
1.50	1.198	3.12	1.353
1.53	1.195	3.26	1.371
1.70	1.214	3.54	1.398
1.85	1.234	3.68	1.418
2.07	1.245	3.85	1.437

varies slowly with temperature; K will therefore vary with T and $e\varphi$. If it were possible to increase the work function of the surface without limit, the equilibrium constant at any temperature would be sufficiently large to satisfy the condition $q=99$. The actual existence of an upper limit to the work function means that there will be a minimum filament temperature below which the conversion of MX to M^+ will be incomplete.

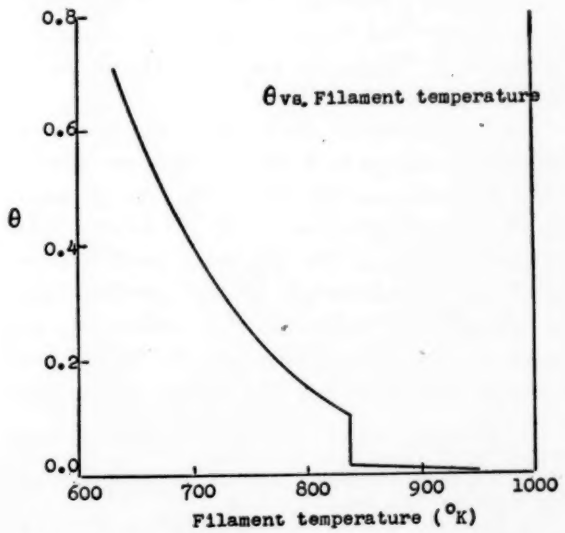


FIG. 3. Adsorption of cesium on tungsten (de Boer).

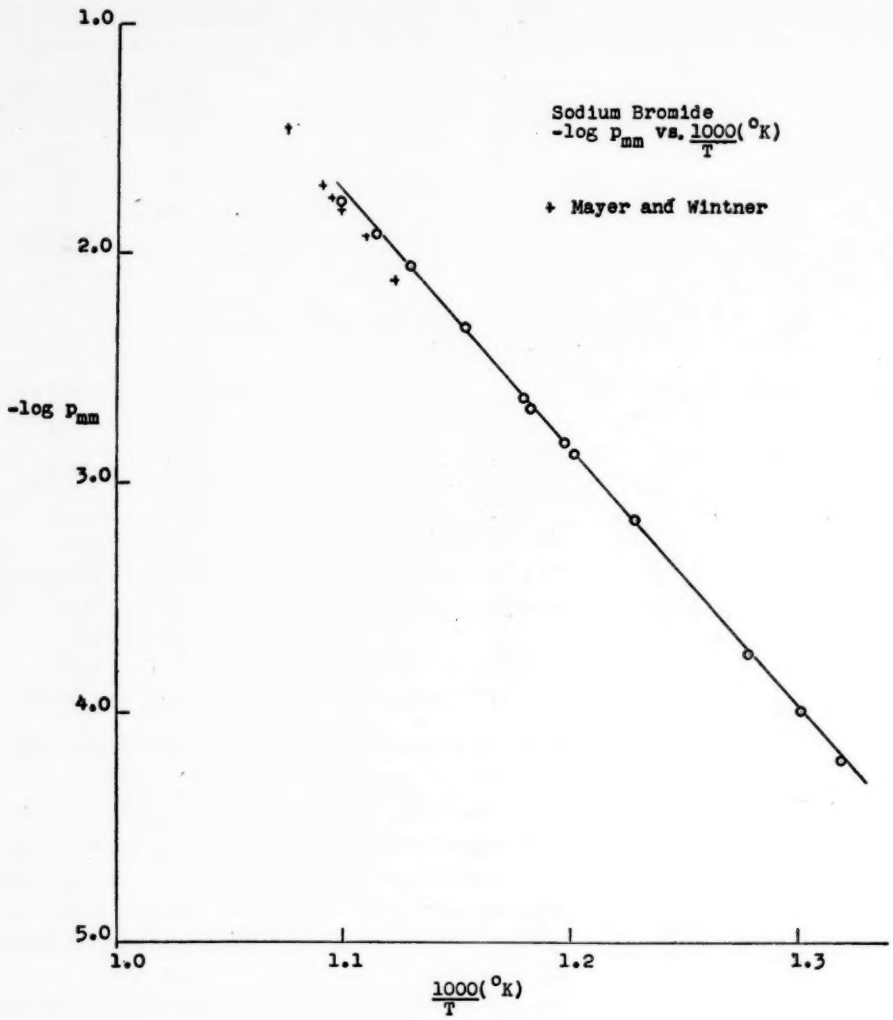


FIG. 4. Vapor pressure *versus* $1000/T$°K (NaBr).

Ionization potentials listed in Table II are taken from Herzberg.[9] Dissociation energies tabulated in Table III are from Herzberg[10] or Mayer and Helmholz.[11]

The experimental filament temperatures for each salt are given in Table IV. Column 3 of this table lists $(e\varphi)_{r=99}$, the work function necessary for 99 percent ionization at T_f; in column 6 are tabulated $(e\varphi)_{q=99}$, the minimum work function satisfying the relation $q=99$ at T_f and the highest pressure of incoming MX molecules. The larger of these two determines the lowest work function sufficient for 99 percent conversion. Under experimental conditions it was possible to maintain a work function of about six volts, which is higher than any of the required work functions. Thus, equilibrium favors conversion of every molecule which hits the filament into the appropriate ion.

2. *Kinetics of the Conversion Reaction*

The following assumptions are made:

a. The rate of reaction is so fast that the reaction goes virtually to completion. There are three possibilities:

(i) The rate is very slow; no conversion.
(ii) There is partial conversion.
(iii) The reaction is very rapid; complete conversion.

[9] G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944).
[10] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).
[11] J. E. Mayer and L. Helmholtz, Zeits. f. Physik **75**, 19 (1932).

The existence of a positive ion current eliminates the first possibility. If the conversion were incomplete, in all probability it would have a temperature coefficient. Only a reaction which had gone virtually to completion would not, since a change from 99.0 to 99.9 percent conversion is a tenfold change without change in result. A plot of the experimental ion current divided by the maximum ion current *versus* filament temperature for KI is shown in curve *I* of Fig. 2. The existence of a plateau indicates that the reaction is actually very fast in this temperature interval.

b. The rate of removal of products is rapid enough to prevent accumulation of metal ions on the surface, with consequent reduction of the work function. When the equilibrium requires incomplete conversion, one may calculate the number of metal ions formed at any given temperature and work function (i.e., for any value of K and r) for any value of the pressure of incoming molecules. One arrives at an expression for n_{M^+}:

$$(n_{M^+})^2+[K/(2\pi\mu kT)^{\frac{1}{2}}]n_{M^+} -[KN_{MX}/(2\pi\mu kT)^{\frac{1}{2}}][r/(1+r)]=0. \quad (5)$$

Thus $\alpha=n_{M^+}/N_{MX}$, the fraction of MX molecules which are converted to M^+ ions under these conditions, may be calculated. α for KI has been evaluated as a function of temperature, assuming a constant work function $e\varphi=5.15$ volts, the work function required for $r>99$ at 1800°K. The oxygen coating strips at high temperatures, lowering the work function. Under the conditions of these experiments, stripping

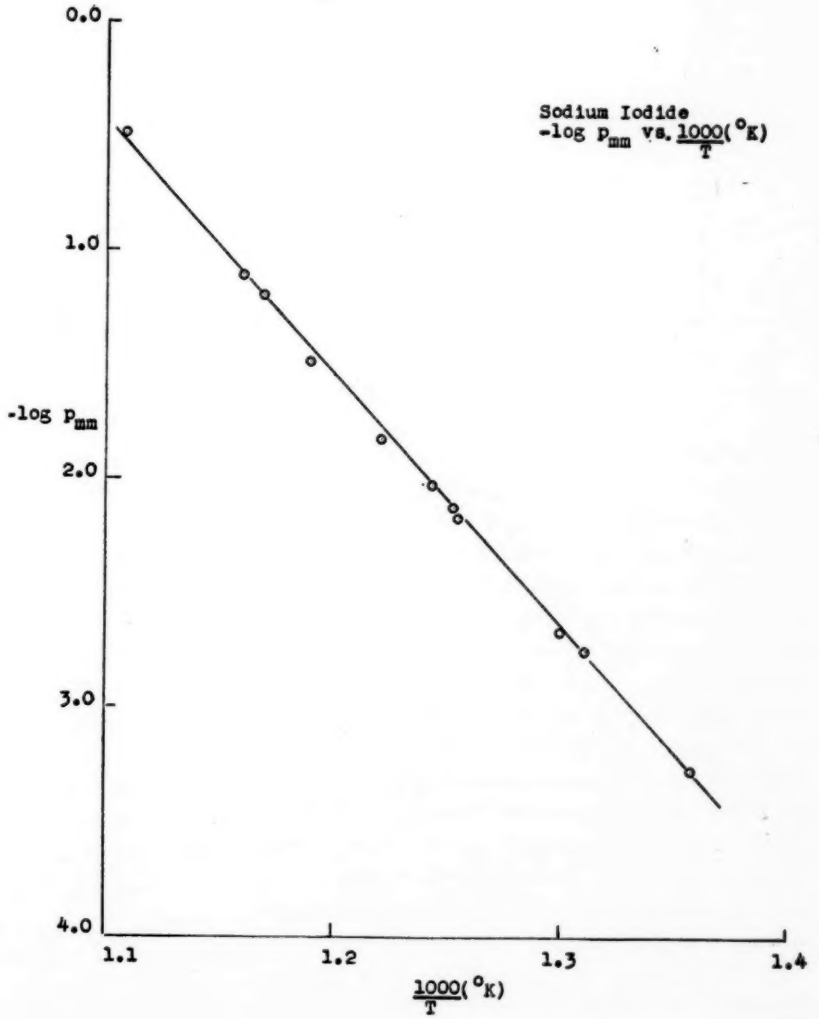


FIG. 5. Vapor pressure *versus* $1000/T$°K (NaI).

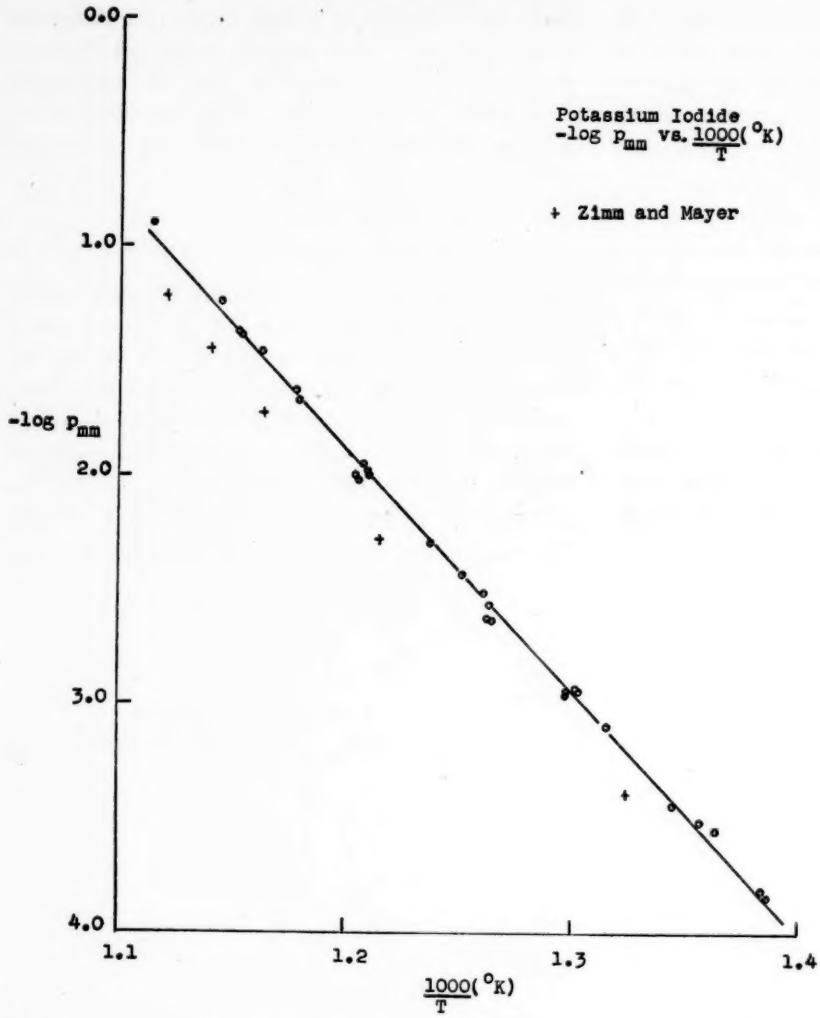


FIG. 6. Vapor pressure *versus* $1000/T^{\circ}$K (KI).

did not occur under 2000°K. The results of this calculation are plotted in curve II of Fig. 2.

A comparison of the experimental curve I and the theoretical curve II in Fig. 2 shows that in the case of KI the shift in the equilibrium does not account for the sharp drop in ion current at low filament temperatures. This phenomenon is probably due to the fact that desorption of metal ions is slow at low temperatures. Since the adsorption energy for metal ions on an oxidized tungsten filament is probably very large, the layer of metal ions will disappear in a very small temperature range above some critical temperature, and the work function of the filament will increase abruptly. This is illustrated by Fig. 3 taken from de Boer[12] which shows the variation of θ, the fraction of tungsten surface covered by adsorbed cesium, with increasing filament temperature, when the cesium is desorbed as ions. According to Taylor and Langmuir,[6] with a given pressure of cesium and with a sufficiently strong accelerating field for ions to overcome space charge there is a critical temperature T_c, above which every cesium atom that strikes the filament escapes as an ion; below T_c, ion emission is very small. The plateau in curve I of Fig. 2 implies a high enough work function and a rapid removal of metal ions in this temperature range.

Therefore it is possible to choose the experimental filament conditions so that the assumption of complete conversion of MX to M^+ on the filament is valid. In these experiments, precautions were taken to have sufficient oxygen

[12] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, Teddington, 1935).

present (using a capillary leak when necessary) to coat the filament and increase its work function. For each salt, the positive ion current at some constant oven temperature was measured as a function of filament temperature, and the vapor pressure measurements were made in the temperature range of the plateau.

c. In order to measure the positive ion current, a potential of −45 to −67.5 volts was put on the plates to overcome ion space charge. To eliminate the effects of stray currents, the galvanometer deflection was first measured with the shutter closed, and the additional deflection when the shutter was opened was assumed to be due entirely to the positive ions. The deflections with closed shutter rarely exceeded ten percent of the ion deflection.

V. MATERIALS

The sodium and potassium salts were prepared by recrystallizing C.P. grade salts from distilled water and drying them in a vacuum oven. The cesium salts were prepared by adding a small excess of the appropriate redistilled C.P. acid to C.P. cesium carbonate (Maywood Chemical Works) which had been recrystallized from absolute alcohol, precipitating the salt, and drying it in a vacuum oven.

The presence of a highly volatile impurity in the salt would give a very high apparent vapor pressure, but its concentration would change during the course of the run, and the resulting pressure would drift with time. The results of measurements on the same sample made on different days agreed with each other within the

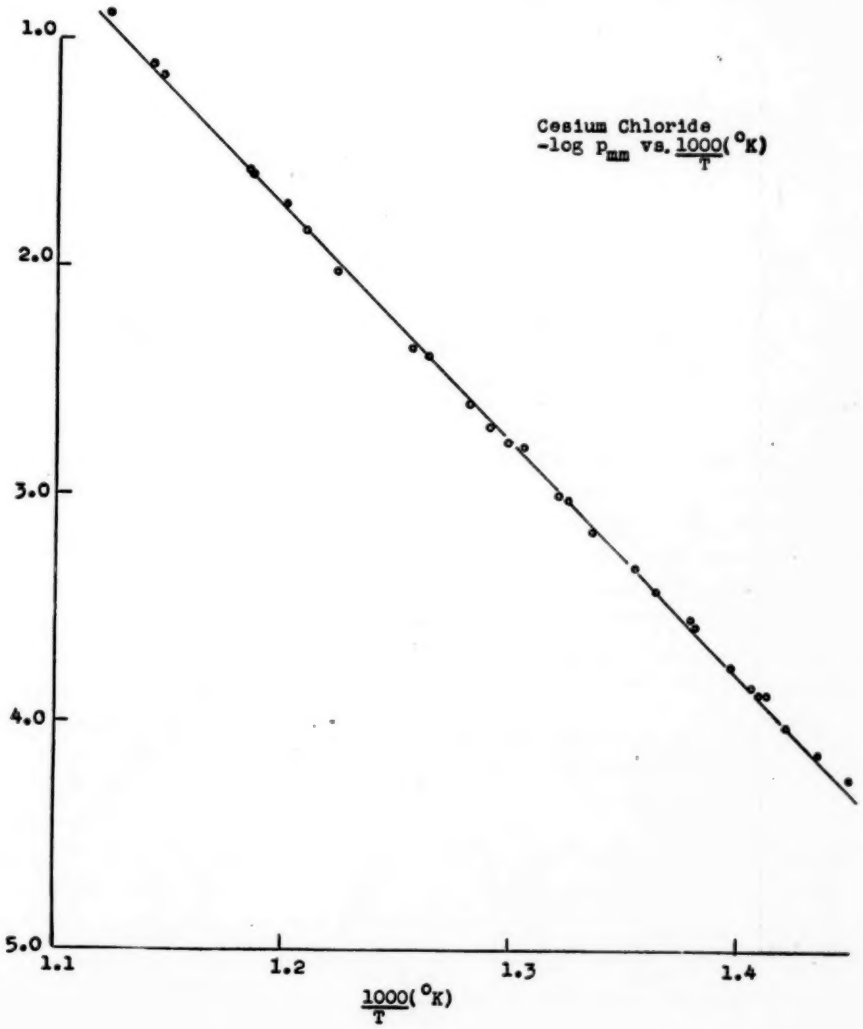


FIG. 7. Vapor pressure *versus* $1000/T°K$ (CsCl).

experimental error, and low temperature data could be repeated after keeping the sample at high temperatures for several hours.

VI. PRIMARY RESULTS

The experimental data are tabulated in Table V and plotted in Figs. 4 and 9. The data are well fitted by the equation:

$$\log p_{mm} = C - A(1000/T) + 5/2 \log(1000/T). \quad (6)$$

The term $5/2 \log(1000/T)$ arises from an estimate of the difference of heat capacities between the gas and crystal. The exact value of the ΔC_p term is unimportant, since it represents only a small correction term. An average value of $\Delta C_p = -5/2R$ for the temperature range 500°K to 1000°K has been used.

The constants in Eq. (6) have been evaluated by the method of least squares and are tabulated in Table VI. The curves in Figs. 4 to 9 have been drawn using the constants in Eq. (6).

VII. SOURCES OF ERROR

The sources of error in p are:

A. Geometry: ±2.9 percent; distance from hole to filament: R±0.5 percent; radius of hole: r±1.1 percent; length of filament: 1±1.0 percent; diameter of filament: d±1.5 percent.

B. Ion current: ±2.8 percent; measurement of galvanometer deflection: ±2 percent; incomplete reaction: ±0.3 percent; scattering correction: ±2 percent.

C. Temperature: ±0.2 percent; maximum error: ±2 percent; probable error: ±0.2 percent.

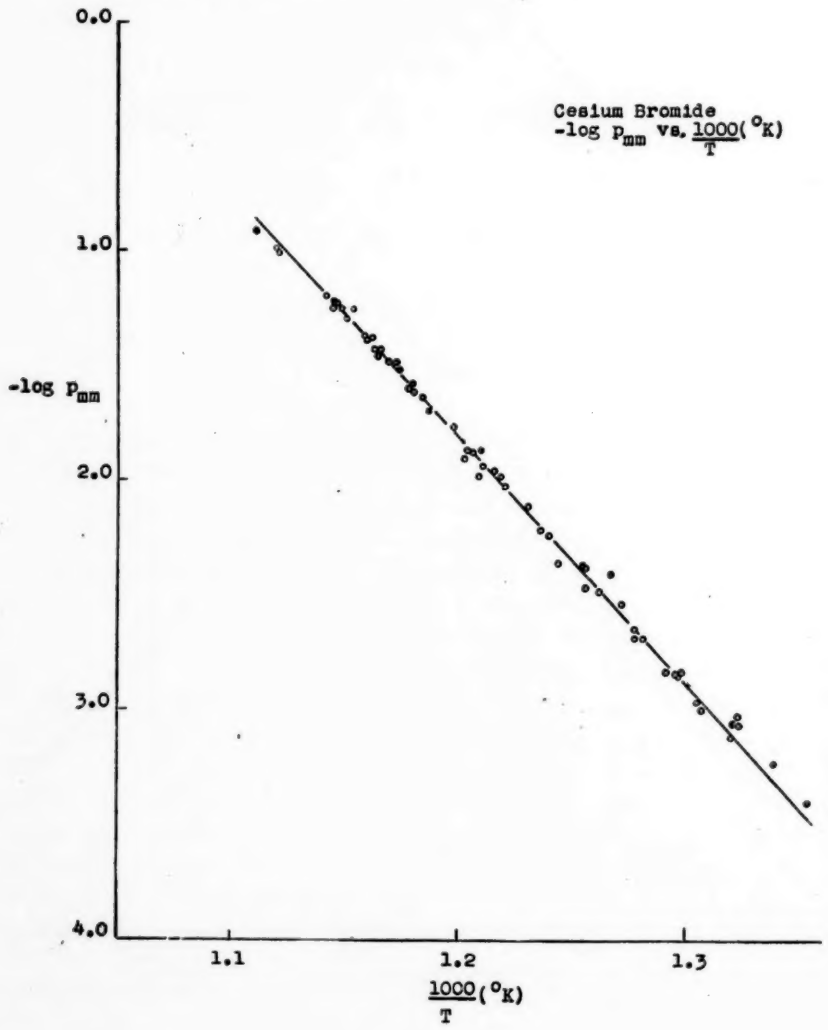


FIG. 8. Vapor pressure *versus* 1000/T°K (CsBr).

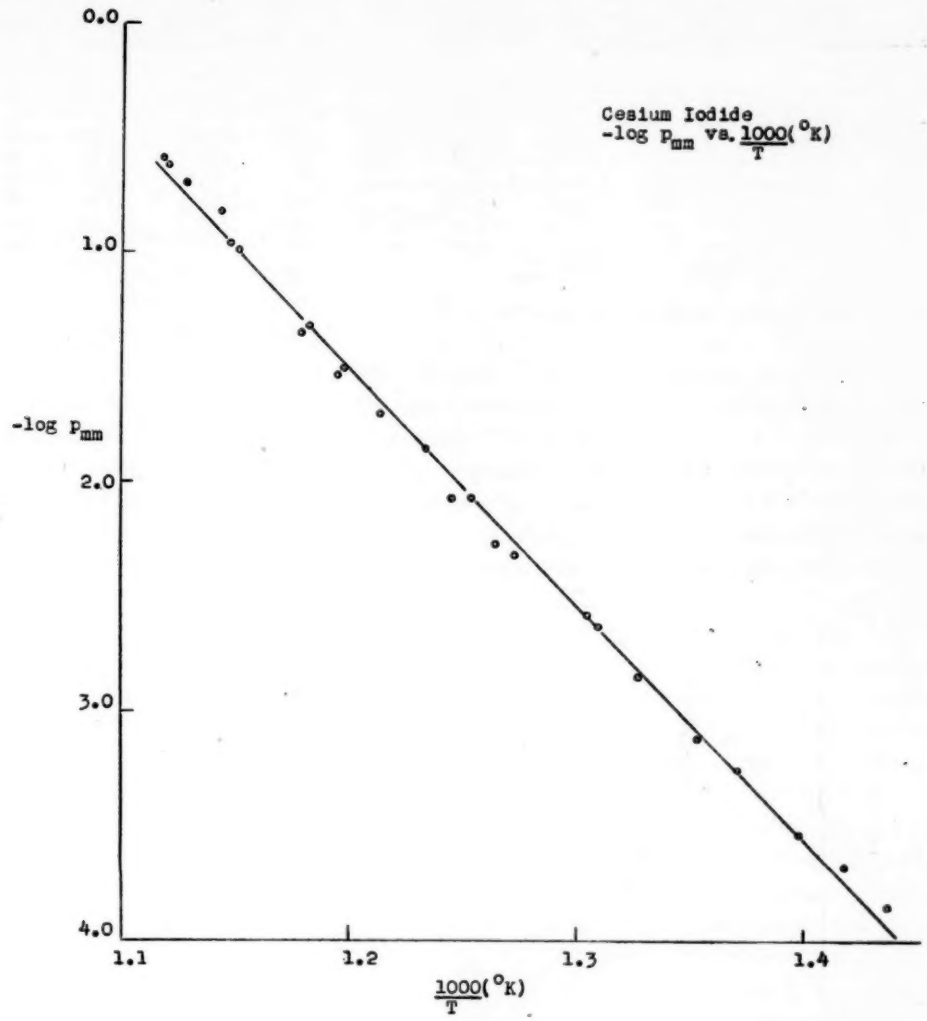


FIG. 9. Vapor pressure *versus* $1000/T°K$ (CsI).

The probable error in p is ± 4.0 percent. Therefore, the probable error in $\ln p$ is ± 0.040.

VIII. DISCUSSION OF RESULTS

Cesium chloride exists in two crystalline modifications. The low temperature form is a body-centered lattice; at 733°K x-ray data[13,14] show a transition to a face-centered lattice. It is expected that the energy difference between these two cubic forms is small. From x-ray measurements, the heat of transition ΔH_t is estimated as 1.8 kcal.[13] Thermal data give a ΔH_t value of 1.34 kcal.[15] There is no observable break in the vapor pressure curve of cesium chloride (see Fig. 7). The probable error in the slope of the line including only those points below the transition temperature is 3.1 percent. The accuracy of these measurements would only be sufficient to say that the heat of transition probably does not exceed 3.1 percent of ΔH_{vap} or 1.5 kcal.

Additional data on the vapor pressure of cesium bromide which have not been used in

TABLE VI. Constants to be used in Eq. (6).

Salt	A	Standard deviation of A	C
NaBr	12.003	0.083	11.347
NaI	11.895	0.14	12.525
KI	11.455	0.097	11.660
CsCl	11.076	0.062	11.346
CsBr	11.421	0.079	11.676
CsI	11.193	0.066	11.726

[13] G. Wagner and L. Lippert, Zeits. f. physik. Chemie **B31**, 263 (1936).
[14] C. D. West, Zeits. f. Krist. **88**, 94 (1934).
[15] International Critical Tables **5**, 207.

TABLE VII. Heat content in kcal./mole.

Salt	ΔH_{800}	H_{gas} $T=800$	ω_0[a] wave no.	$H_{crystal}$ $T=800$	ΔH_0
NaBr	50.93±0.35	6.79	133.9	9.38	53.52
NaI	50.43±0.91	6.83	117.0	9.65	53.25
KI	48.42±0.46	6.92	98.0	9.65	51.15
CsCl	46.69±0.26	6.90	98.0	9.76	49.55
CsBr	48.26±0.33	6.97	74.6	10.21	51.50
CsI	47.23±0.28	7.01	(61)*	9.82	50.04

* Estimated.
[a] R. B. Barnes, Zeits. f. Physik 75, 723 (1932).

TABLE VIII. Entropies in cal./degree.

Salt	S_{gas}° $T=800$	$-\ln p_{mm}$ $T=800$	S_{gas} $T=800$	ΔS_{800}	$S_{crystal}$ $T=800$
NaBr	79.60	7.86	95.21	63.66	31.55
NaI	81.33	4.84	90.94	63.04	27.90
KI	83.55	5.57	94.60	60.53	34.07
CsCl	83.17	5.20	93.50	58.36	35.14
CsBr	85.71	5.43	96.49	60.35	36.14
CsI	87.53	4.65	96.81	59.04	37.77

the evaluation of the constants in Eq. (6) are plotted in Fig. 10. These peculiar results are not explanable. Two ovens were used in these measurements (Oven I with a hole diameter of approximately 0.1 cm and Oven II with a hole diameter of approximately 0.01 cm) and the data were taken at two filament temperatures (1400°K and 1800°K) using many different samples of salt.

The portion of curve I labeled *AB* corresponds to Fig. 8 and was obtained in both ovens with fresh samples which had never been heated above T_c (approximately 875°K). The material looked powdered before and after heating. *BC* shows the rapid rise in vapor pressure when the

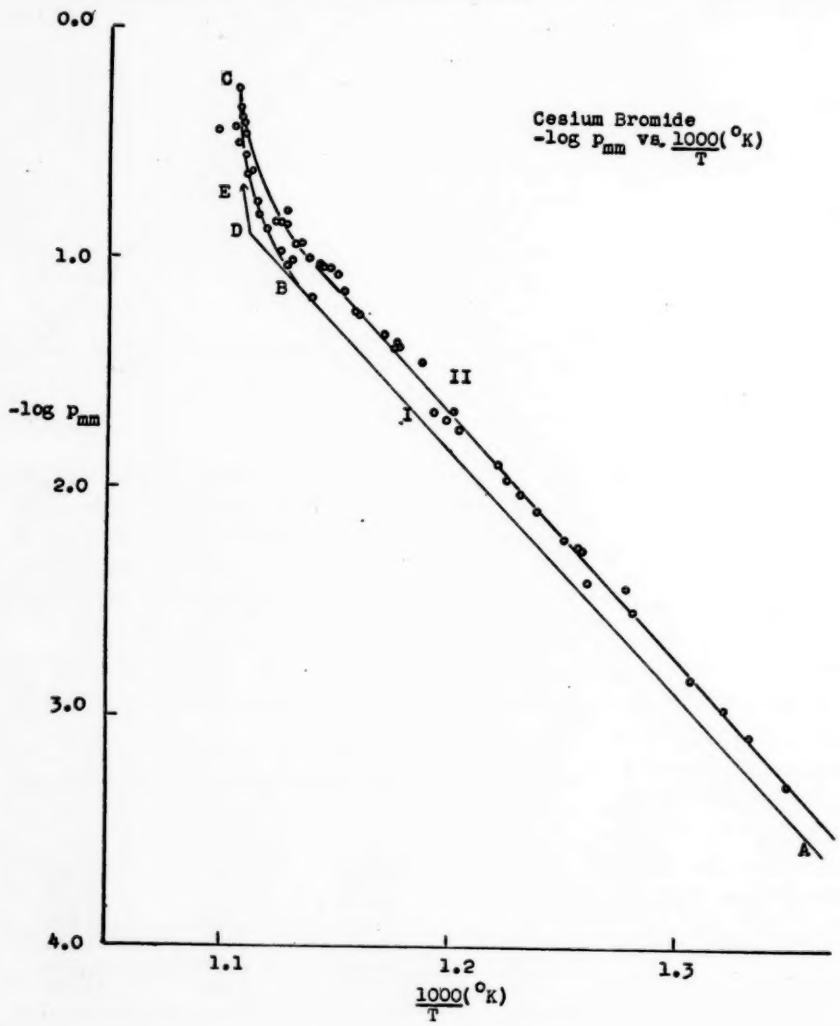


FIG. 10. Vapor pressure *versus* $1000/T$°K (CsBr).

salt was heated above T_c in Oven I. The data then fall on curve II when the salt is cooled and remain on curve II throughout all subsequent heating and cooling. This material now appears sintered, but there is no indication that the sample had melted ($T_{m.p.}=909.2°K$). No difference in structure was found from x-ray powder pictures of the original powdered salt, crushed sintered material, and small (but uncrushed) fragments of sintered material. Previous x-ray investigators had looked for a transition in cesium bromide but had never found one.[13,14] Microchemical analysis showed these materials to be the same within the error of the determination (original sample: 37.55 percent Br; sintered material: 37.98 percent Br). *BD* was obtained when fresh samples were heated above T_c in Oven II and is a continuation of *AB*. This material was still powdered after heating. *DE* shows the extremely rapid rise at 900°K (an increase in pressure from 0.1 to 7 mm in 2.5°) when the sample was heated in Oven II. On cooling the data could be represented by curve II and the material was sintered. There is no evidence that the salt, which leaves the oven at a very great rate in the region of anomalous pressures, has condensed on the outer surface of the oven or radiation shields.

The data of Mayer and Wintner for sodium bromide are plotted in Fig. 4. In Fig. 6 the results of Mayer and Zimm for potassium iodide are given. Their entropy of vaporization agrees with ours to 0.5 percent, but the vapor pressures obtained in these measurements are 1.55 times those of Zimm and Mayer. Results of measurements on two samples of potassium iodide, one prepared in this laboratory and the other in the phosphor research laboratory at the Polytechnic Institute of Brooklyn, were the same within experimental error.

TABLE IX. Entropies in cal./degree.

Salt	$S_{cryst}(T=800) - S_{cryst}(T=298)$	$S_{crystal}$ $T=298$	$S_{gas}°$ $T=298$
NaBr	12.76	18.79	70.85
NaI	13.15	14.74	72.61
KI	12.92	21.15	74.80
CsCl	13.10	22.04	74.35
CsBr	13.73	22.41	76.87
CsI	12.80	24.97	78.72

IX. DERIVED RESULTS

The measurements of this research permit the calculation of $\Delta F_T°$ for the vaporization of the salt (from the vapor pressure at any one temperature) and the ΔH_T of vaporization from the relation:

$$d \ln p/d(1/T) = -\Delta H_T/R.$$

From these one may calculate the entropy difference between vapor and crystal. The heats of vaporization at 800°K are listed in Table VII; the entropies of vaporization at 800°K are given in Table VIII.

The entropies of the crystal and gas may be calculated from statistical equations[16] but with uncertain accuracy. The equilibrium internuclear distance in the gaseous molecule is known in all cases.[17] Since the frequencies of the gaseous molecule are known in some cases,[6] and a reasonably good estimate of the frequencies has been made in others,[18] the accuracy with which the vapor entropies may be obtained is good. The calculation of the crystal entropies, however, is more uncertain. In order to get good agreement between crystal entropies obtained from heat capacity data and those calculated using the Debye function, it is necessary to use the *reststrahlen* frequency to determine the parameter θ_D. This is theoretically unsound. The use of this as an empirical relationship is limited because few of these reflection frequencies are known. The Nernst-Lindemann equation has a sounder theoretical basis, but does not give as good agreement with experiment. Therefore, the entropy of the crystal was obtained by using the experimental entropy difference between the gas and crystal and the calculated vapor entropy. The values of the entropies of the gas and crystal at 800°K are tabulated in Table VIII. Because heat capacity data are lacking above room temperature for most of these crystals, extrapolation of the crystal entropy from 800°K to 298°K has been made, using the heat capacity equations estimated by Kelley.[19] In the case of sodium bromide, a long extrapolation of the

[16] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).
[17] E. J. W. Verwey and J. H. Boer, Rec. trav. chem. **59**, 633 (1940).
[18] W. Gordy, J. Chem. Phys. **14**, 305 (1946).
[19] K. K. Kelley, U. S. Bur. Mines Bull., 371 (1934).

TABLE A1. Quantities used in calculating gaseous entropies: $I_e=\mu r_0^2$, $B_e=h/8\pi^2 I_e c$, $\omega^*=\omega_e-2\omega_e x_e$, $B_0=B_e-(\alpha/2)$, $\alpha/2=3(B_e^2/\omega_e)((\omega_e x_e/B_e)^{\frac{1}{2}}-1)$.

Salt	Reduced mass μ grams $\times 10^{23}$	Frequency ω_e cm^{-1}	Anharmonicity correction $\omega_e x_e$	Interatomic[a] distance r_{1800} cm $\times 10^8$	Equilibrium[b] distance r_0 cm $\times 10^8$	Moment of inertia I_e $I_e \times 10^{38}$	$B_e \times 10^2$	$uT=hc\omega^*/k$	$\sigma T=B_0 hc/k$	$\gamma=B_e/\omega_e$ $\gamma \times 10^4$
Sodium bromide	2.965	315[b]	1.15[b]	2.64	2.59	1.989	14.07	450.4	0.2019	4.47
Sodium iodide	3.232	286[b]	0.75[b]	2.90	2.84	2.607	10.74	409.4	0.1543	3.76
Potassium iodide	4.962	212[b]	0.7[b]	3.23	3.16	4.955	5.649	302.9	0.08110	2.66
Cesium chloride	4.643	226[c]	(0.7)*	3.06	3.00	4.179	6.698	323.8	0.09620	2.96
Cesium bromide	8.278	168[c]	(0.5)*	3.14	3.07	7.802	3.588	240.3	0.05154	2.13
Cesium iodide	10.77	137[c]	(0.4)*	3.41	3.33	11.94	2.344	195.7	0.03367	1.71

* Estimated.
[a] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, Phys. Rev. **52**, 968 (1937).
[b] See reference 10.
[c] See reference 18.

TABLE A2. $S_k°$ = translational entropy at 1 mm pressure, S_v = vibrational entropy, S_r = rotational entropy, S_e = correction to the entropy due to anharmonicity and stretching.

Salt	$S_k°/R$	S_v/R	S_r/R	S_e/R	$S°/R$
			$T=800°K$		
NaBr	29.144	1.588	9.286	0.058	40.076
NaI	29.698	1.681	9.556	0.019	40.954
KI	29.860	1.977	10.198	0.032	42.067
CsCl	29.881	1.912	10.028	0.060	41.881
CsBr	30.233	2.207	10.652	0.067	43.159
CsI	30.533	2.410	11.077	0.079	44.099
			$T=298°K$		
Salt	$S_k°/R$	S_v/R	S_r/R	S_e/R	$S°/R$
NaBr	26.673	0.688	8.298	0.015	35.674
NaI	27.234	0.757	8.568	0.003	36.562
KI	27.397	1.019	9.256	0.010	37.662
CsCl	27.403	0.964	9.040	0.029	37.436
CsBr	27.760	1.242	9.664	0.040	38.706
CsI	28.059	1.439	10.090	0.048	39.636

experimental heat capacity equation was necessary. The entropy of the crystal and the calculated entropy of the gas at 298°K are given in Table IX.

Because sufficient heat capacity data are unavailable, it was necessary to calculate the heat content of the crystal. The heat content of the crystal at $T=298$ was calculated in the following way:

$$H_T-H_0=\int_0^T C_v dT+\frac{2}{5}aT^{5/2},$$

where the last term arises from the Lindemann-Magnus approximation for C_p-C_v. The Nernst-Lindemann heat capacity equation was used to evaluate C_v:

$$C_v=(3nR/2)f_E(\theta_E/T)+(3nR/2)f_E(\theta_E/2T),$$

where f_E = Einstein function, $\theta_E=h\nu_0/k$, ν_0 = optical absorption frequency, and n = number of atoms per molecule of crystal. ΔH for the interval $T=298$ to $T=800$ was evaluated using the heat capacity equations of Kelley. The values of $H_c=H_T-H_0$ are tabulated in Table VII. The difference between the heat content of the crystal and the gas at 800°K added to the experimental heat of vaporization at 800°K gives ΔH_0, the heat of vaporization at absolute zero. These results are given in Table VII.

X. ACKNOWLEDGMENT

The authors wish to thank Dr. Joseph E. Mayer for suggesting the problem and for many helpful discussions.

APPENDIX

The entropy of the gaseous alkali halide molecules at 298°K and 800°K have been evaluated by the usual statistical mechanical equations.[16] The quantities used in these calculations are listed in Table A.1. In Table A.2 are given the various contributions to the entropy and the total standard state entropy (pressure 1mm).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

On Certain Integrals Useful in Molecular Orbital Calculations*

ROBERT G. PARR** AND BRYCE L. CRAWFORD, JR.
School of Chemistry, University of Minnesota, Minneapolis, Minnesota

(Received May 19, 1948)

Previous calculations of integrals which enter computations by the method of antisymmetric molecular orbitals are reviewed, several new integrals are evaluated, and a master table of integrals is given.

IN a paper entitled "Antisymmetric molecular orbitals. II. Calculation of integrals," Sklar and Lyddane[1] summarized the evaluation of some of the integrals over atomic orbitals which occur in quantitative calculations by the method of antisymmetric molecular orbitals. In the present paper, the work of Sklar and Lyddane and previous investigators will be critically reviewed, and certain new integrals will be evaluated.

The integrals to be considered involve $2p$ atomic orbitals on two identical nuclei: A and B. If these nuclei are taken as origins for the Cartesian coordinate systems (x_a,y_a,z_a) and (x_b,y_b,z_b) [$x_a=x_b$, $y_a=y_b$; z's along internuclear axis], and the polar coordinate systems (a,θ_a,ϕ) and (b,θ_b,ϕ), respectively, the three orthonormal, real, hydrogen-like $2p$ wave functions for electron ν on A and B may be written[2] in atomic units[3] as

$$\begin{aligned} a(\nu)&=(Z^5/32\pi)^{\frac{1}{2}}y_a\exp(-Za_\nu/2)\\ &=(Z^5/32\pi)^{\frac{1}{2}}a_\nu\exp(-Za_\nu/2)\sin\theta_{a\nu}\cos\phi_\nu,\\ a_s(\nu)&=(Z^5/32\pi)^{\frac{1}{2}}x_a\exp(-Za_\nu/2)\\ &=(Z^5/32\pi)^{\frac{1}{2}}a_\nu\exp(-Za_\nu/2)\sin\theta_{a\nu}\sin\phi_\nu,\\ a_r(\nu)&=(Z^5/32\pi)^{\frac{1}{2}}z_a\exp(-Za_\nu/2)\\ &=(Z^5/32\pi)^{\frac{1}{2}}a_\nu\exp(-Za_\nu/2)\cos\theta_{a\nu}; \end{aligned} \tag{1}$$

and

$$\begin{aligned} b(\nu)&=(Z^5/32\pi)^{\frac{1}{2}}y_b\exp(-Zb_\nu/2)\\ &=(Z^5/32\pi)^{\frac{1}{2}}b_\nu\exp(-Zb_\nu/2)\sin\theta_{b\nu}\cos\phi_\nu,\\ b_s(\nu)&=(Z^5/32\pi)^{\frac{1}{2}}x_b\exp(-Zb_\nu/2)\\ &=(Z^5/32\pi)^{\frac{1}{2}}b_\nu\exp(-Zb_\nu/2)\sin\theta_{b\nu}\sin\phi_\nu,\\ b_r(\nu)&=(Z^5/32\pi)^{\frac{1}{2}}z_b\exp(-Zb_\nu/2)\\ &=(Z^5/32\pi)^{\frac{1}{2}}b_\nu\exp(-Zb_\nu/2)\cos\theta_{b\nu}; \end{aligned} \tag{2}$$

where Z is an effective nuclear charge and the subscript ν denotes coordinates of electron ν.

The integrals are of several types. First, there are the *overlap integrals*[4]

$$S_{\alpha\beta}=\int\alpha(1)\beta(1)d\nu_1, \tag{3}$$

where α is one of $\{a,a_s,a_r\}$ and β one of $\{b,b_s,b_r\}$. Secondly, there are the *Coulomb integrals*

$$(\alpha_1\alpha_2;\beta_1\beta_2)=\int\alpha_1(1)\beta_1(2)(2/r_{12})\alpha_2(1)\beta_2(2)d\nu_1,d\nu_2, \tag{4}$$

the *hybrid Coulomb-exchange integrals*

$$(\alpha_1\beta_1;\beta_2\beta_3)=\int\alpha_1(1)\beta_2(2)(2/r_{12})\beta_1(1)\beta_3(2)d\nu_1d\nu_2, \tag{5}$$

and the *exchange integrals*

$$(\alpha_1\beta_1;\alpha_2\beta_2)=\int\alpha_1(1)\alpha_2(2)(2/r_{12})\beta_1(1)\beta_2(2)d\nu_1d\nu_2, \tag{6}$$

where the α_i are members of the set $\{a,a_s,a_r\}$, the β_i are members of the set $\{b,b_s,b_r\}$, and r_{12} is the distance between electrons 1 and 2. For zero internuclear distance, these integrals reduce to

* This paper is based partly on a thesis submitted by Robert G. Parr to the Graduate School of the University of Minnesota, August, 1947, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and partly on research supported by the Office of Naval Research, U. S. Navy, through Contract N5ori-147 with the University of Minnesota.

** Present address: Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[1] A. L. Sklar and R. H. Lyddane, J. Chem. Phys. **7**, 374 (1939).

[2] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944), pp. 89–90.

[3] Distances in units of the first Bohr radius $a_0=0.5292$A; energies in units of $e^2/2a_0=2.1792\times10^{-11}$ ergs $=13.602$ ev, where e is the charge on an electron.

[4] $d\nu_\nu$ denotes element of volume in coordinates of electron ν; unless otherwise specified, integrations are over all space.

mononuclear integrals of the form

$$(\alpha_1\alpha_2;\alpha_3\alpha_4) = \int \alpha_1(1)\alpha_3(2)(2/r_{12})\alpha_2(1)\alpha_4(2)dv_1dv_2. \quad (7)$$

Finally, there are the *Coulomb penetration* integrals

$$(A:\beta\beta) = -\int \mathbf{H}_A^*(1)\beta(1)\beta(1)dv_1 \quad (8)$$

and the *exchange penetration integrals*

$$(A:\alpha\beta) = -\int \mathbf{H}_A^*(1)\alpha(1)\beta(1)dv_1, \quad (9)$$

where $\mathbf{H}_A^*(1)$ is the spherically symmetric potential energy operator for electron 1 in the field of neutral atom A.

The various integrals are given in Table I as function of the screening constant Z and the parameter

$$\rho = ZR, \quad (10)$$

where R is the internuclear distance; their evaluation is described in detail below.

OVERLAP INTEGRALS

The only non-vanishing integrals of the form (3) are $S_{ab} \equiv S_{a_sb_s}$ and $S_{a_rb_r}$. To evaluate these, one may introduce elliptical coordinates

$$\lambda = (a+b)/R, \quad \mu = (a-b)/R, \quad \phi \text{ as above.} \quad (11)$$

One then finds[5]

$$S_{ab} = \exp(-\rho/2)[1+(\rho/2) + (\rho^2/10)+(\rho^3/120)], \quad (12)$$

and

$$S_{a_rb_r} = \exp(-\rho/2)[1+(\rho/2)+(\rho^2/20) - (\rho^3/60)-(\rho^4/240)]. \quad (13)$$

Values of S_{ab} and $S_{a_rb_r}$ calculated from these formulas are given in Table I.

MONONUCLEAR INTEGRALS

Sklar and Lyddane gave to the integral

$$(aa;aa) = \int a(1)a(2)(2/r_{12})a(1)a(2)dv_1dv_2, \quad (14)$$

which represents the mutual potential energy of two $2p$ electrons in the same $2p$ orbital on the same atom, the value $0.3881Z$. Actually, $Z^{-1}(aa;aa) = 0.3914$,[6] as will now be shown.

TABLE I. Values of integrals (atomic units[e]).

Integral ρ	0	3[c]	4[c]	5[c]	6	7	8	8.37	9	10	12	14.5	16.7	20
$Z^{-1}(aa;bb)$	0.3914	0.3476	0.3151	0.2890	0.2616	0.2367	0.2163	0.2086[a]	0.1972	0.1806	0.155	0.131	0.115	0.097
$Z^{-1}(aa;b_sb_s)$	0.3492	0.3164	0.2909	0.2710	0.2484	0.2273	0.2097	0.2036[a]	0.1928	0.1774				
$Z^{-1}(aa_s;bb_s)$	0.0211	0.0156	0.0121	0.0090	0.0066	0.0047	0.0033	0.0025[a]	0.0022	0.0016				
$Z^{-1}(aa;b_rb_r)$	0.3492	0.338	0.324	0.305	0.285	0.262	0.241		0.220	0.200				
$Z^{-1}(aa_r;bb_r)$	0.0211	0.0056	−0.0009	−0.0044	−0.0064	−0.0067	−0.0062		−0.0053	−0.0042				
$Z^{-1}(a_ra_r;b_rb_r)$	0.3914	0.359	0.346	0.332	0.315	0.296	0.278		0.252	0.231				
$Z^{-1}(ab;bb)$	0.3914				0.1538			0.0766		0.0448		0.0087		
$Z^{-1}(ab;b_sb_s)$	0.3492				0.1399			0.0704		0.0415		0.0082		
$Z^{-1}(ab_s;bb_s)$	0.0211				0.0069			0.0031		0.0016		0.0003		
$Z^{-1}(ab;ab)$	0.3914				0.073			0.022		0.0082	0.0031	0.0006	0.0001	0.0000
$Z^{-1}(ab;a_sb_s)$	0.3492				0.066			0.020[b]		0.0074[b]				
$Z^{-1}(ab_s;ab_s)$	0.0211		0.005	0.005	0.0035	0.0025		0.0012[b]		0.0004[b]				
$Z^{-1}(ab_r;ab_r)$	0.0211	0.043	0.030	0.039	0.028	0.021	0.015		0.010	0.006				
$Z^{-1}(ab_r;a_rb)$	−0.0211	−0.043	−0.030	−0.039	−0.028	−0.021	−0.015		−0.010	−0.006				
$Z^{-1}(A:bb)$[d]	0.5859				0.0773			0.01976		0.00703	0.00182	0.00031	0.0$_4$6	0.0$_4$46
$Z^{-1}(A:ab)$[d]	0.5859				0.1200			0.04364		0.02090				
S_{ab}	1.0000				0.46800			0.25995		0.16396	0.08874	0.03883	0.01798	
$S_{a_rb_r}$	1.0000											−0.15356	−0.08946	

[a] Interpolated.
[b] Extrapolated.
[c] Values in these columns should probably be adjusted slightly to smooth the transition to the limiting $\rho=0$ values. Such adjustment would be in accord with the statement made by Bartlett (p. 522 of reference 5) that his values may be somewhat in error for small ρ.
[d] A = carbon.
[e] See reference 3.

[5] J. H. Bartlett, Phys. Rev. **37**, 507 (1931).
[6] In a letter to one of the authors (RGP) dated August 30, 1947, Dr. Lyddane agrees to this value.

In polar coordinates (15) reads

$$(aa;aa)=(Z^5/32\pi)^2\int \exp(-Za_1)a_1^2 \times\sin^2\theta_{a1}\cos^2\phi_1 dv_1\cdot(2/r_{12}) \times\exp(-Za_2)a_2^2\sin^2\theta_{a2}\cos^2\phi_2 dv_2. \quad (15)$$

Now[7]

$$(2/r_{12})=2\sum_{n=0}^{\infty}\sum_{m=-n}^{n}(n-|m|)![(n+|m|)!]^{-1} \times a_<^n a_>^{-n-1}\cdot P_n^{|m|}(\cos\theta_{a1}) \times P_n^{|m|}(\cos\theta_{a2})\exp[im(\phi_1-\phi_2)], \quad (16)$$

where

$$a_<=\min.\{a_1,a_2\},\quad a_>=\max.\{a_1,a_2\}, \quad (17)$$

and the quantities

$$P_n^m(x)=2^{-n}(n!)^{-1}(1-x^2)^{m/2} \times[d^{n+m}(x^2-1)^n/dx^{n+m}] \quad (18)$$

are the associated Legendre functions. Also,

$$dv_\nu=a_\nu^2\sin\theta_{a\nu}da_\nu d\theta_{a\nu}d\phi_\nu. \quad (19)$$

Therefore

$$(aa;aa)=2(Z^5/32\pi)^2\sum_{n=0}^{\infty}\sum_{m=n}^{n}(n-|m|)! \times[(n+|m|)!]^{-1}\cdot\int\cos^2\phi_1\cos^2\phi_2 \times\exp[im(\phi_1-\phi_2)]d\phi_1 d\phi_2 \times\int\sin^3\theta_{a1}\sin^3\theta_{a2}P_n^{|m|}(\cos\theta_{a1}) \times P_n^{|m|}(\cos\theta_{a2})d\theta_{a1}d\theta_{a2}\cdot\int\exp(-Za_1) \times\exp(-Za_2)a_1^4a_2^4a_<^n a_>^{-n-1}da_1da_2. \quad (20)$$

The integral over ϕ_1 and ϕ_2 is

$$\int\cos^2\phi_1\cos^2\phi_2\exp[im(\phi_1-\phi_2)]d\phi_1d\phi_2 =\left[\int_0^{2\pi}\cos^2\phi_1\cos m\phi_1 d\phi_1\right]^2 =\begin{cases}\pi^2 \text{ if } m=0,\\ \pi^2/4 \text{ if } |m|=2,\\ 0 \text{ otherwise;}\end{cases} \quad (21)$$

[7] Reference 3, Appendix V.

the integral over θ_{a1} and θ_{a2} is[8]

$$\int\sin^3\theta_{a1}\sin^3\theta_{a2}P_n^{|m|}(\cos\theta_{a1})P_n^{|m|}(\cos\theta_{a2})d\theta_{a1}d\theta_{a2} =\left[\int_{-1}^{1}(1-x^2)P_n^{|m|}(x)dx\right]^2 =\begin{cases}16/9 \text{ if } m=0 \text{ and } n=0,\\ 16/225 \text{ if } m=0 \text{ and } n=2,\\ 256/25 \text{ if } |m|=2 \text{ and } n=2,\\ 0 \text{ if } m=0 \text{ and } n\neq 0 \text{ or } 2,\\ 0 \text{ if } |m|=2 \text{ and } n\neq 2.\end{cases} \quad (22)$$

Hence

$$(aa;aa)=2(Z^5/32)^2\Big\{(16/9)\int\exp(-Za_1) \times\exp(-Za_2)a_1^4a_2^4a_>^{-1}da_1da_2+[(16/225) +(1/4)(2/4!)(256/25)]\int\exp(-Za_1) \times\exp(-Za_2)a_1^4a_2^4a_>^{-3}a_<^2da_1da_2\Big\} =(Z/7200)\Big\{25\int_0^\infty\exp(-u)u^4g_{5,1}(u)du +4\int_0^\infty\exp(-u)u^4g_{7,3}(u)du\Big\}, \quad (23)$$

where

$$g_{5,1}(u)=(1/u)\int_0^u\exp(-V)V^4dV +\int_u^\infty\exp(-V)V^3dV, \quad (24)$$

$$g_{7,3}(u)=(1/u^3)\int_0^u\exp(-V)V^6dV +u^2\int_u^\infty\exp(-V)VdV.$$

But

$$g_{5,1}(u)=(1/u)\{24-\exp(-u)[u^3+6u^2 +18u+24]\}, \quad (25)$$
$$g_{7,3}(u)=(5/u^3)\{144-\exp(-u)[u^5+6u^4 +24u^3+72u^2+144u+144]\},$$

[8] See, for example, Whittaker and Watson, *Modern Analysis* (The Macmillan Company, New York, 1943), p. 324.

so that

$$\int_0^\infty \exp(-u)u^4 g_{5,1}(u)du = 837/8,$$
$$\int_0^\infty \exp(-u)u^4 g_{7,3}(u)du = 405/8, \tag{26}$$

and

$$(aa;aa) = (4509/11520)Z = 0.3914Z. \tag{27}$$

The integrals $(aa;a_sa_s) \equiv (aa;a_ra_r)$ and $(aa_s;aa_s) \equiv (aa_r;aa_r)$ can be found similarly. These differ from $(aa;aa)$ only in the integral over ϕ_1 and ϕ_2; in the case of $(aa;a_sa_s)$ there enters

$$\int \cos^2\phi_1 \sin^2\phi_2 \exp[im(\phi_1-\phi_2)]d\phi_1 d\phi_2$$
$$= \left[\int_0^{2\pi} \cos^2\phi_1 \cos m\phi_1 d\phi_1\right] \times \left[\int_0^{2\pi} \sin^2\phi_2 \cos m\phi_2 d\phi_2\right]$$
$$= \begin{cases} \pi^2 \text{ if } m=0, \\ -\pi^2/4 \text{ if } |m|=2, \\ 0 \text{ otherwise;} \end{cases} \tag{28}$$

in the case of $(aa_s;aa_s)$ there enters

$$\int \sin\phi_1 \cos\phi_1 \sin\phi_2 \cos\phi_2 \exp[im(\phi_1-\phi_2)]d\phi_1 d\phi_2$$
$$= \left[(1/2)\int_0^{2\pi} \sin 2\phi_1 \sin m\phi_1 d\phi_1\right]^2$$
$$= \begin{cases} \pi^2/4 \text{ if } |m|=2, \\ 0 \text{ otherwise.} \end{cases} \tag{29}$$

Thus

$$(aa;a_sa_s) = (Z/7200)\left\{25\int_0^\infty \exp(u)u^4 g_{5,1}(u)du - 2\int_0^\infty \exp(-u)u^4 g_{7,3}(u)du\right\}, \tag{30}$$

$$(aa_s;aa_s) = (Z/7200)\left\{3\int_0^\infty \exp(-u)u^4 g_{7,3}(u)du\right\},$$

and

$$(aa;a_sa_s) = (4023/11520)Z = 0.3492Z,$$
$$(aa_s;aa_s) = (243/11520)Z = 0.0211Z. \tag{31}$$

(27) and (31) establish most of the limiting $\rho=0$ values which are listed in Table I.

COULOMB AND EXCHANGE INTEGRALS

The non-zero Coulomb integrals are $(aa;bb)$, $(aa;b_sb_s)$, $(aa;b_rb_r)$, $(aa_s;bb_s)$, $(aa_r;bb_r)$ and $(a_ra_r;b_rb_r)$; the non-zero exchange integrals are $(ab;ab)$, $(ab_s;ab_s) \equiv (ab_s;a_sb)$, $(ab_r;ab_r)$, $(ab;a_sb_s)$, $(ab;a_rb_r)$, $(ab_r;a_rb)$ and $(a_rb_r;a_rb_r)$. These may be expressed as follows in terms of the integrals i_k of Bartlett:[5]

$$(aa;bb) = i_1 + (1/2)i_7, \quad (ab;ab) = i_2 + (1/2)i_8;$$
$$(aa;b_sb_s) = i_1 - (1/2)i_7, \quad (ab;a_sb_s) = i_2 - (1/2)i_8;$$
$$(aa_s;bb_s) = (1/2)i_7,$$
$$(ab_s;ab_s) = (ab_s;a_sb) = (1/2)i_8; \tag{32}$$
$$(aa;b_rb_r) = i_3, \quad (ab;a_rb_r) = i_4;$$
$$(aa_r;bb_r) = i_5, \quad (ab_r;ab_r) = i_6, \quad (ab_r;a_rb) = i_{11};$$
$$(a_ra_r;b_rb_r) = i_9, \quad (a_rb_r;a_rb_r) = i_{10}.$$

The first pair of these formulas was given by Goeppert-Mayer and Sklar.[9]

Table I gives values of the Coulomb integrals $(\alpha_1\alpha_2;\beta_1\beta_2)$ and those exchange integrals $(\alpha_1\beta_1;\alpha_2\beta_2)$ which are multiples if i_6, i_8, and i_{11}, calculated from Bartlett's values for the i_k.[5,10,11] Also given in Table I are Sklar and Lyddane's values for the Coulomb integral $(aa;bb)$, for $10 < \rho \leqslant 20$, and the exchange integral $(ab;ab)$, for $0 < \rho \leqslant 20$. Bartlett did not tabulate i_2 explicitly, but Sklar and Lyddane appear to have dug it out of his paper, allowing them to calculate $(ab;ab) = i_2 + (1/2)i_8$. They found values for large ρ "by developing approximation formulas which are valid for large ρ and by extrapolating Bartlett's tables for small quantities."

Bartlett failed to tabulate i_4 and i_{10}, so that the exchange integrals $(ab;a_rb_r)$ and $(a_rb_r;a_rb_r)$ are not included in Table I.

HYBRID COULOMB-EXCHANGE INTEGRALS

The hybrid Coulomb-exchange integrals are somewhat troublesome. The only ones which

[9] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938).

[10] The signs of i_5, i_6, and i_7 are wrong in reference 5; this was pointed out by W. H. Furry and J. H. Bartlett in Phys. Rev. 38, 211 (1932).

[11] This procedure was first carried out for $(aa;bb)$ and $(ab;ab)$ by Goeppert-Mayer and Sklar (reference 9) [corrected by Sklar and Lyddane (reference 1)].

will be considered here are

$$(ab;bb)=\int a(1)b(2)(2/r_{12})b(1)b(2)dv_1dv_2,$$

$$(ab;b_sb_s)=\int a(1)b_s(2)(2/r_{12})b(1)b_s(2)dv_1dv_2, \quad (33)$$

$$(ab_s;bb_s)=\int a(1)b(2)(2/r_{12})b_s(1)b_s(2)dv_1dv_2.$$

These will be evaluated by the method which was applied by Sklar and Lyddane to the first of them—expansion of $(2/r_{12})$ in spherical harmonics followed by successive integrations over ϕ_1, v_2, and the remaining coordinates of electron 1.

Substituting into

$$(ab;bb)=(Z^5/32\pi)^2\int \exp[-(Z/2)(a_1+b_1)]a_1b_1 \times\sin\theta_{a1}\sin\theta_{b1}\cos^2\phi_1dv_1\cdot(2/r_{12}) \times\exp(-Zb_2)b_2^2\sin^2\theta_{b2}\cos^2\phi_2dv_2 \quad (34)$$

the expansion of $(2/r_{12})$ in spherical harmonics about nucleus B (Eq. (16) with a replaced by b) and the elements of volume $dv_1=(dv_1/d\phi_1)d\phi_1$, $dv_2=b_2^2\sin\theta_{b2}db_2d\theta_2d\phi_2$, one finds

$$(ab;bb)=2(Z^5/32\pi)^2\sum_{n=0}^{\infty}\sum_{m=-n}^{+n}(n-|m|)! \times[(n+|m|)!]^{-1}\int\cos^2\phi_1\cos^2\phi_2 \times\exp[im(\phi_1-\phi_2)]d\phi_1d\phi_2 \times\int\sin^3\theta_{b2}P_n^{|m|}(\cos\theta_{b2})d\theta_{b2} \times\int\exp(-Zb_2)b_<^nb_>^{-n-1}b_2^4db_2 \times\int\exp[-(Z/2)(a_1+b_1)]a_1b_1\sin\theta_{a1} \times\sin\theta_{b1}P_n^{|m|}(\cos\theta_{b1})(dv_1/d\phi_1). \quad (35)$$

By virtue of (21), (22), and the relations

$$\int_0^\infty\exp(-Zb_2)b_>^{-1}b_2^4db_2=(1/Z^4)g_{5,1}(Zb_1),$$

$$\int_0^\infty\exp(-Zb_2)b_<^2b_>^{-3}b_2^4db_2=(1/Z^4)g_{7,3}(Zb_1), \quad (36)$$

(35) becomes

$$(ab;bb)=(2/Z^4)(Z^5/32)^2 \times\int\exp[-(Z/2)(a_1+b_1)]a_1b_1 \times\sin\theta_{a1}\sin\theta_{b1}\cdot\{(4/3)g_{5,3}(Zb_1) -[(4/15)P_2(\cos\theta_{b1}) -(1/15)P_2^2(\cos\theta_{b1})]g_{7,3}(Zb_1)\} \cdot(dv_1/d\phi_1), \quad (37)$$

which is in agreement with Sklar and Lyddane's Eq. (7). Similarly, making use of (28) and (29), one obtains

$$(ab;b_sb_s)=(2/Z^4)(Z^5/32)^2 \times\int\exp[-(Z/2)(a_1+b_1)]a_1b_1 \times\sin\theta_{a1}\sin\theta_{b1}\cdot\{(4/3)g_{5,1}(Zb_1) -[(4/15)P_2(\cos\theta_{b1}) +(1/15)P_2^2(\cos\theta_{b1})]g_{7,3}(Zb_1)\} \cdot(dv_1/d\phi_1) \quad (38)$$

and

$$(ab_s;bb_s)=(2/Z^4)(Z^5/32)^2 \times\int\exp[-(Z/2)(a_1+b_1)]a_1b_1 \times\sin\theta_{a1}\sin\theta_{b1}\cdot\{(1/15) \times P_2^2(\cos\theta_{b1})g_{7,3}(Zb_1)\}(dv_1/d\phi_1). \quad (39)$$

As independent coordinates of electron 1, it is convenient to take ϕ_1,

$$\alpha=Za_1 \quad \text{and} \quad \beta=Zb_1. \quad (40)$$

With $\rho=ZR$ and $dv_1=(1/\rho Z^3)\alpha d\alpha\beta d\beta d\phi_1$, (37)–(39) then become

$$Z^{-1}(ab;bb)=(1/7680\rho^3)\int\exp[-(1/2)(\alpha+\beta)] \times[2(\alpha^2\beta^2+\alpha^2\rho^2+\beta^2\rho^2)-(\alpha^4+\beta^4+\rho^4)] \times\{5g_{5,1}(\beta)-[1+(9/16\beta^2\rho^2)(\alpha^4+\beta^4+\rho^4) -(9/8\beta^2\rho^2)(\alpha^2\beta^2+\alpha^2\rho^2+\beta^2\rho^2)]g_{7,3}(\beta)\} \cdot\alpha d\alpha\beta d\beta, \quad (41)$$

$$Z^{-1}(ab;b_sb_s)=(1/7680\rho^3)\int\exp[-(1/2)(\alpha+\beta)] \times[2(\alpha^2\beta^2+\alpha^2\rho^2+\beta^2\rho^2)-(\alpha^4+\beta^4+\rho^4)] \times\{5g_{5,1}(\beta)-[1+(3/16\beta^2\rho^2)(\alpha^4+\beta^4+\rho^4) -(3/8\beta^2\rho^2)(\alpha^2\beta^2+\alpha^2\rho^2+\beta^2\rho^2)]g_{7,3}(\beta)\} \cdot\alpha d\alpha\beta d\beta, \quad (42)$$

and

$$Z^{1-}(ab_s;bb_s)=(\tfrac{1}{2})[Z^{-1}(ab;bb)-Z^{-1}(ab;b_sb_s)]. \quad (43)$$

Equation (41) is equivalent to Sklar and Lyddane's Eq. (8).

According to Sklar and Lyddane, one must now indulge in a "considerable amount of rearrangement and integration by parts." In terms of the integrals

$$I(s,t)=(1/2)\exp(\rho/2)\int \exp[-(1/2)(\alpha+\beta)] \times\alpha^s\beta^t d\alpha d\beta = I(t,s),$$

$$J(s,t)=(3/2)\exp(\rho/2) \times\int \exp[-(1/2)(\alpha+3\beta)]\alpha^s\beta^t d\alpha d\beta,$$

$$K(s)=(1/2)\exp(\rho/2)\int \exp[-(1/2)(\alpha+3\beta)] \times[\exp(\beta)-1]\alpha^s\beta^{-1} d\alpha d\beta,$$

$$A_s=\exp(2\rho)\int_\rho^\infty \exp(-2\alpha)\alpha^s d\alpha = \int_0^\infty \exp(-2x)(x+\rho)^s dx, \quad (44)$$

$$B_s=\exp(-\rho)\int_0^\rho \exp(\alpha)\alpha^s d\alpha = \int_0^\rho \exp(-x)(\rho-x)^s dx,$$

$$C_s=\exp(\rho)\int_\rho^\infty \exp(-\alpha)\alpha^s d\alpha = \int_0^\infty \exp(-x)(x+\rho)^s dx,$$

$$D_s=s!\exp(\rho)-C_s=\exp(\rho)\int_0^\rho \exp(-\alpha)\alpha^s d\alpha = \int_0^\rho \exp(x)(\rho-x)^s dx,$$

there result[12]

$$\begin{aligned}
12288\rho^5\exp(\rho/2)Z^{-1}(ab;bb)&=48\textstyle\sum_1-\sum_2 \\
&\quad+9(\textstyle\sum_3+\sum_4+\sum_5+\sum_6),\\
12288\rho^5\exp(\rho/2)Z^{-1}(ab;b_sb_s)&=48\textstyle\sum_1{}^s-\sum_2{}^s \\
&\quad+9(\textstyle\sum_3{}^s+\sum_4{}^s+\sum_5{}^s+\sum_6{}^s),\\
12288\rho^5\exp(\rho/2)Z^{-1}(ab_s;bb_s)&=48\textstyle\sum_1{}^{ss}-\sum_2{}^{ss} \\
&\quad+9(\textstyle\sum_3{}^{ss}+\sum_4{}^{ss}+\sum_5{}^{ss}+\sum_6{}^{ss}),
\end{aligned} \quad (45)$$

[12] Details of the reduction of Eqs. (41)–(43) to Eqs. (45) will be furnished upon request.

where the sums $\sum$ are given by:

$$\begin{aligned}
\textstyle\sum_1&=(162-8\rho^2)I(5,0)+(-108+16\rho^2)\\
&\quad\cdot I(3,2)+(12\rho^2+16\rho^4)I(3,0)\\
&\quad+(27-8\rho^2)I(1,4)+(-60\rho^2+16\rho^4)\\
&\quad\cdot I(1,2)+(66\rho^4-8\rho^6)I(1,0),\\
\textstyle\sum_1{}^s&=(54-8\rho^2)I(5,0)+(-36+16\rho^2)\\
&\quad\cdot I(3,2)+(-60\rho^2+16\rho^4)I(3,0)\\
&\quad+(9-8\rho^2)I(1,4)+(12\rho^2+16\rho^4)\\
&\quad\cdot I(1,2)+(-42\rho^4-8\rho^6)I(1,0);
\end{aligned} \quad (46)$$

$$\begin{aligned}
\textstyle\sum_2&=3J(9,1)+18J(9,0)-12J(7,3)\\
&\quad-72J(7,2)-(288+12\rho^2)J(7,1)\\
&\quad-(864+72\rho^2)J(7,0)+18J(5,5)\\
&\quad+108J(5,4)+(432+12\rho^2)J(5,3)\\
&\quad+(1296+72\rho^2)J(5,2)+(2592+320\rho^2\\
&\quad+18\rho^4)J(5,1)+(2592+1120\rho^2\\
&\quad+108\rho^4)J(5,0)-12J(3,7)-72J(3,6)\\
&\quad-(288-12\rho^2)J(3,5)-(864-72\rho^2)\\
&\quad\cdot J(3,4)-(1728-224\rho^2-12\rho^4)J(3,3)\\
&\quad-(1728-352\rho^2-72\rho^4)J(3,2)\\
&\quad+(192\rho^2+224\rho^4-12\rho^6)J(3,1)\\
&\quad+(192\rho^2+352\rho^4-72\rho^6)J(3,0)\\
&\quad+3J(1,9)+18J(1,8)+(72-12\rho^2)\\
&\quad\cdot J(1,7)+(216-72\rho^2)J(1,6)+(432\\
&\quad-256\rho^2+18\rho^4)J(1,5)+(432-608\rho^2\\
&\quad+108\rho^4)J(1,4)-(960\rho^2-368\rho^4\\
&\quad+12\rho^6)J(1,3)-(960\rho^2-784\rho^4+72\rho^6)\\
&\quad\cdot J(1,2)+(1056\rho^4-256\rho^6+3\rho^8)J(1,1)\\
&\quad+(1056\rho^4-608\rho^6+18\rho^8)J(1,0),
\end{aligned} \quad (47)$$

$$\begin{aligned}
\textstyle\sum_2{}^s&=J(9,1)+6J(9,0)-4J(7,3)-24J(7,2)\\
&\quad-(96+4\rho^2)J(7,1)-(288+24\rho^2)\\
&\quad\cdot J(7,0)+6J(5,5)+36J(5,4)+(144\\
&\quad+4\rho^2)J(5,3)+(432+24\rho^2)J(5,2)\\
&\quad+(864+128\rho^2+6\rho^4)J(5,1)+(864\\
&\quad+544\rho^2+36\rho^4)J(5,0)-4J(3,7)\\
&\quad-24J(3,6)-(96-4\rho^2)J(3,5)-(288\\
&\quad-24\rho^2)J(3,4)-(576-32\rho^2-4\rho^4)\\
&\quad\cdot J(3,3)-(576+224\rho^2-24\rho^4)J(3,2)\\
&\quad-(960\rho^2-32\rho^4+4\rho^6)J(3,1)-(960\rho^2\\
&\quad+224\rho^4+24\rho^6)J(3,0)+J(1,9)\\
&\quad+6J(1,8)+(24-4\rho^2)J(1,7)\\
&\quad+(72-24\rho^2)J(1,6)+(144-64\rho^2\\
&\quad+6\rho^4)J(1,5)+(144-32\rho^2+36\rho^4)\\
&\quad\cdot J(1,4)+(192\rho^2+80\rho^4-4\rho^6)J(1,3)\\
&\quad+(192\rho^2-80\rho^4-24\rho^6)J(1,2)\\
&\quad-(672\rho^4+64\rho^6-\rho^8)J(1,1)\\
&\quad-(672\rho^4+32\rho^6-6\rho^8)J(1,0);
\end{aligned}$$

$$\sum_3 = -3K(9)+(288+12\rho^2)K(7) -(416\rho^2+18\rho^4)K(5)-(32\rho^4-12\rho^6) \cdot K(3)+(160\rho^6-3\rho^8)K(1), \quad (48)$$

$$\sum_3{}^s = -K(9)+(96+4\rho^2)K(7)-(224\rho^2 +6\rho^4)K(5)+(160\rho^4+4\rho^6)K(3) -(32\rho^6+\rho^8)K(1);$$

$$\sum_4 = (443/840)\rho^9-(303/140)\rho^8 -(8276/105)\rho^7-1086\rho^5 -7208\rho^4-27045\rho^3-69708\rho^2 -1886895/16)\rho-(791505/8), \quad (49)$$

$$\sum_4{}^s = (443/2520)\rho^9-(101/140)\rho^8 +(676/105)\rho^7-106\rho^5 -1208\rho^4-6615\rho^3-21252\rho^2 -(628965/16)\rho-(263835/8);$$

$$\sum_5 = -3C_8+(6+27\rho)C_7+(264-54\rho -96\rho^2)C_6-(1800\rho-192\rho^2-168\rho^3)C_5 +(4864\rho^2-336\rho^3-144\rho^4)C_4 -(6656\rho^3-288\rho^4-48\rho^5)C_3 +(4736\rho^4-96\rho^5)C_2-1408\rho^5C_1, \quad (50)$$

$$\sum_5{}^s = -C_8+(2+9\rho)C_7+(88-18\rho-32\rho^2)C_6 -(600\rho-64\rho^2-56\rho^3)C_5 +(1536\rho^2-112\rho^3-48\rho^4)C_4 -(1792\rho^3-96\rho^4-16\rho^5)C_3 +(896\rho^4-32\rho^5)C_2-128\rho^5C_1;$$

$$\sum_6 = \exp(-\rho)[9(A_8+D_8)+(18-81\rho)(A_7+D_7) -(264+162\rho-288\rho^2)(A_6+D_6) +(1800\rho+576\rho^2-504\rho^3)(A_5+D_5) -(4864\rho^2+1008\rho^3-432\rho^4)(A_4+D_4) +(6656\rho^3+864\rho^4-144\rho^5)(A_3+D_3) -(4736\rho^4+288\rho^5)(A_2+D_2) +1408\rho^5(A_1+D_1)], \quad (51)$$

$$\sum_6{}^s = \exp(-\rho)[3(A_8+D_8)+(6-27\rho)(A_7+D_7) -(88+54\rho-96\rho^2)(A_6+D_6) +(600\rho+192\rho^2-168\rho^3)(A_5+D_5) -(1536\rho^2+336\rho^3-144\rho^4)(A_4+D_4) +(1792\rho^3+288\rho^4-48\rho^5)(A_3+D_3) -(896\rho^4+96\rho^5)(A_2+D_2) +128\rho^5(A_1+D_1)];$$

$$\sum_k{}^{ss} = (1/2)(\sum_k - \sum_k{}^s). \quad (52)$$

The first of Eqs. (45) does not agree with Sklar and Lyddane's Eq. (9) for $Z^{-1}(ab;bb)$. The following changes are necessary in the latter to bring it into accord with the former:[13]

(1) Change $(1/2)\sum_3$ to $-\sum_3$.

(2) In $\sum_2$, change $\rho^8 J(1,1)-(\rho^6-\rho^8)J(1,0)$ to $(1/16)\rho^8 J(1,1)-[(38/3)\rho^6-(3/8)\rho^8]J(1,0)$.

(3) In $\sum_4$, change $-(107/9)\rho^4-(4195/8)\rho^3 -(14279/6)\rho^2-(637065/128)\rho-(277815/64)$ to $(901/9)\rho^4+(3005/8)\rho^3+(5809/6)\rho^2 +(209655/128)\rho+(87945/64)$.

(4) In $\sum_6$, change $(14/3)\rho^3(A_4+D_4)$ to $14\rho^3(A_4+D_4)$.

Some of these errors are doubtless misprints.[14]

Values of $Z^{-1}(ab;bb)$, $Z^{-1}(ab;b_sb_s)$ and $Z^{-1}(ab_s;bb_s)$, calculated from (45) and the tables of Sklar and Lyddane for the $I(s,t)$, $J(s,t)$, and $K(s)$,[15] are given in Table I. These integrals fall nicely between the corresponding Coulomb and exchange integrals, as they should.

PENETRATION INTEGRALS

The Coulomb penetration integral

$$(A:bb) = -\int \mathbf{H}_A{}^*(1)b(1)b(1)dv_1 \quad [A=\text{carbon}], \quad (53)$$

and the exchange penetration integral

$$(A:ab) = -\int \mathbf{H}_A{}^*(1)a(1)b(1)dv_1 \quad [A=\text{carbon}], \quad (54)$$

have been evaluated by Sklar and Lyddane [in Sklar and Lyddane's notation, $(A:bb)=Q_{22}(\rho)$, $(A:ab)=Q_{12}(\rho)$], but the numerical values quoted by those authors do not agree with the formulas given by them.

If the 1s electrons on carbon A are treated as if on the nucleus,[16] the potential $\mathbf{H}_A{}^*(1)$ on electron 1 due to the carbon atom A is (in c.g.s.

[13] The $\sum$'s defined in the present paper are multiples of the ones employed by Sklar and Lyddane.

[14] In a letter of one of the authors (reference 6), Dr. Lyddane states: "The errors . . . in $(ab;bb)/Z$ . . . are all typographical with one exception; the value of $\sum_4$ is wrong in our paper."

[15] For $\rho=14.5$, $I(5,0)=2.4864\times10^6$, not 2.4864×10^7 as Sklar and Lyddane state.

[16] This method of evaluation was outlined by M. Goeppert-Mayer and A. L. Sklar (reference 9) (see also Sklar and Lyddane, reference 2).

units)

$$\mathbf{H}_A^*(1) = -(4e^2/a_1) + (1/a_1)\int_0^{a_1} e^2\sigma(a)a^2da + \int_{a_1}^{\infty} e^2\sigma(a)ada, \quad (55)$$

where a_1 is the distance between electron 1 and nucleus A, and

$$\sigma(a) = 4\pi[|\psi_{2s}|^2+|\psi_{2px}|^2+|\psi_{2py}|^2+|\psi_{2pz}|^2] = \int[|\psi_{2s}|^2+|\psi_{2px}|^2+|\psi_{2py}|^2+|\psi_{2pz}|^2](dv/a^2da). \quad (56)$$

But

$$\int_0^{\infty}\sigma(a)a^2da = \int[|\psi_{2s}|^2+|\psi_{2px}|^2+|\psi_{2py}|^2+|\psi_{2pz}|^2]dv = 4, \quad (57)$$

so that *in c.g.s. units*

$$\mathbf{H}_A^*(1) = -(e^2/a_1)\int_{a_1}^{\infty}(a-a_1)\sigma(a)ada \quad (58)$$

and *in atomic units*[3]

$$\mathbf{H}_A^*(1) = -(2/a_1)\int_{a_1}^{\infty}(a-a_1)\sigma(a)ada. \quad (59)$$

Here[2]

$$\sigma(a) = (Z^3/4)\exp(-Za)[2-2(Za)+(Za)^2]. \quad (60)$$

Hence (in atomic units)

$$\mathbf{H}_A^*(1) = -(1/2a_1)\exp(-Za_1)[16+12(Za_1)+4(Za_1)^2+(Za_1)^3]. \quad (61)$$

Substitution into (53) of (61) and the first of Eqs. (2) and integration by the method applied above to the overlap integrals yield the formula

$$Z^{-1}(A:bb) = (1/1920)\exp(-\rho)[(4/7)\rho^5+(67/7)\rho^4+86\rho^3+461\rho^2+1125(\rho+1)] \quad [A=\text{carbon}]. \quad (62)$$

Similarly, integration of (54) by the method applied above to the hybrid Coulomb-exchange integrals gives

$$Z^{-1}(A:ab) = (1/384\rho^3)\exp(-\rho/2) \times\{-J(5,3)-4J(5,2)-12J(5,1)-16J(5,0) +2J(3,5)+8J(3,4)+24J(3,3)+32J(3,2) -J(1,7)-4J(1,6)-12J(1,5)-16J(1,4) +\rho^2[2J(3,3)+8J(3,2)+24J(3,1)+32J(3,0) +2J(1,5)+8J(1,4)+24J(1,3)+32J(1,2)] -\rho^4[J(1,3)+4J(1,2)+12J(1,1) +16J(1,0)]\} \quad [A=\text{carbon}]. \quad (63)$$

For $\rho=0$, each of these integrals reduces to

$$Z^{-1}(A:aa) = 1125/1920 = 0.5859 \quad [A=\text{carbon}]. \quad (64)$$

Equation (62) differs from Sklar and Lyddane's Eq. (18) by a factor of 2 and the appearance of $86\rho^3$ in place of $46\rho^3$; Eq. (63) differs from Sklar and Lyddane's Eq. (19) by a factor of 2. Equations (62) and (63) reproduce exactly Sklar and Lyddane's numerical values, however, indicating that those authors employed the correct equations in their computations.[17-19] These values are included in Table I.

Similar methods could be applied to the calculation of $(A:b_rb_r)$ and $(A:a_rb_r)$.

ACKNOWLEDGMENTS

The authors wish to thank Dr. R. H. Lyddane for verification of some of the results reported here, and Dr. C. E. Sun and Mr. M. V. King for help in various phases of the work.

[17] Dr. Lyddane has confirmed this.

[18] V. Griffing, J. Chem. Phys. **15**, 421 (1947), noted that the values given in the first row of Sklar and Lyddane's Table VI are larger than those calculated from their Eq. (18), but laid the blame on the calculations rather than on the equation.

[19] Other misprints in the Sklar-Lyddane paper include:
In Eq. (6) for Z read Z^5, for b_2 read b_2^2.
In Eq. (8), for $(5/\beta)$ read $(5/\beta^3)$.
In Eq. (15), for $(1+e^{-\rho})$ read $(1+e^{+\rho})$.
In Eq. (16), for $(1/2)sA_s-1$ read $(1/2)sA_{s-1}$.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

The Reaction of Atomic Hydrogen with Acetylene

E. L. TOLLEFSON* AND D. J. LE ROY
Department of Chemistry, University of Toronto, Toronto, Canada
(Received June 1, 1948)

The thermal dissociation of hydrogen on hot tungsten filaments has been used in the investigation of the reaction of atomic hydrogen with acetylene. A quantitative method has been developed for the detection of atomic hydrogen at pressures of the order of 10^{-3} mm. The catalytic effect of acetylene on the recombination of atomic hydrogen has been studied and the rate constant of the rate-determining step calculated to be 8.6×10^{-14} molecules^{-1} cm^3 sec.$^{-1}$ at 25°C. In contrast with results obtained by the discharge tube method, small amounts of hydrogenated products are formed.

INTRODUCTION

THE reaction of atomic hydrogen with acetylene has been studied by a number of investigators using the discharge tube method of Wood and Bonhoeffer.[1–5] The nature of the discharge is such that a flow system must be used in which the total pressure is of the order of 0.5 mm. In most experiments the pressure of atomic hydrogen was from 0.1 to 0.2 mm, and under these conditions it was found that while small amounts of acetylene greatly accelerated the consumption of hydrogen atoms, no products other than hydrogen and acetylene were detected. Similar results were obtained with atomic deuterium,[4] but in this case there was a rapid exchange. The collision yield of deuterization was estimated to correspond to an activation energy of less than 5 kcal. per mole and two possible mechanisms were suggested to explain the results:

$$\text{I}\quad \begin{cases} H+C_2H_2=C_2H_3, & (1)\\ H+C_2H_3=C_2H_2+H_2. & (2)\end{cases}$$

$$\text{II}\quad \begin{cases} H+C_2H_2=C_2H+H_2, & (3)\\ H+C_2H=C_2H_2. & (4)\end{cases}$$

Using the method of photosensitization to produce atomic hydrogen, Le Roy and Steacie[5] found as products, ethane, ethylene, butane, and a polymer of the approximate composition $(C_2H_4)_n$. Since the pressure of atomic hydrogen was lower than that obtained by the discharge tube method by several orders of magnitude, they concluded that hydrogenated products could be produced only in the presence of large H_2:H ratios. On the basis of Mechanism I vinyl radicals could then partake in the reaction

$$C_2H_3+H_2=C_2H_4+H \qquad (5)$$

or

$$C_2H_3+H_2=C_2H_5. \qquad (6)$$

If Mechanism II obtains the corresponding reaction would be

$$C_2H+H_2=C_2H_3, \qquad (7)$$

followed by either (5) or (6). Vinyl radicals would play an important part in either case.

In order to obtain a clearer insight into the elementary reactions involved it seemed desirable to develop a method capable of yielding pressures of atomic hydrogen which would overlap those previously used. In addition it was essential to devise some means of measuring these pressures.

EXPERIMENTAL DETAILS

Despite Langmuir's classical work on the formation of atomic hydrogen by thermal dissociation on tungsten filaments this method has only recently been applied to chemical investigations.[6] Relatively wide variations in condi-

* Present address, Division of Chemistry, National Research Laboratories, Ottawa, Ontario.

[1] K. F. Bonhoeffer and P. Harteck, Zeits. f. physik. Chemie **139**, 64 (1928).

[2] H. v. Wartenberg and G. Schultze, Zeits. f. physik. Chemie **B2**, 1 (1929).

[3] K. H. Geib and P. Harteck, Ber. **66**, 1315 (1933).

[4] K. H. Geib and E. W. R. Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935); Trans. Roy. Soc. (Canada) III, 29, 91 (1935).

[5] D. J. Le Roy and E. W. R. Steacie, J. Chem. Phys. **12**, 369 (1944).

[6] J. P. W. Houtman, K. Van Den Berg and P. M. Heertjes, Rec. trav. Chim. **62**, 672 (1943).

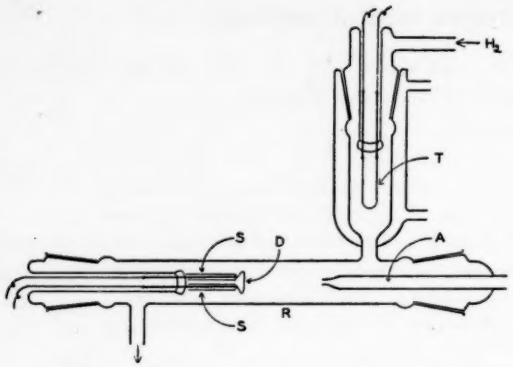


FIG. 1. Apparatus for the production and detection of atomic hydrogen.

tions are made possible by controlling the temperature of the filament and the pressure and flow rate of the hydrogen.

The part of the system used to produce and detect atomic hydrogen is shown in Fig. 1. The tungsten filament, T, 0.004 inch in diameter and from one and a half to two inches long, was spot-welded to conventional nickel-tungsten lead-in wires. The filament assembly was sealed to a standard 24/40 ground joint lubricated with Apiezon N grease; the filament chamber and ground joint were surrounded by a water jacket. The current was controlled manually and the filament temperature measured to $\pm 50°C$ by means of an optical pyrometer. Purified hydrogen entered at H_2, and the mixture of atomic and molecular hydrogen then passed into the reaction tube, R, through a jet approximately 8 mm in diameter. The opening in the acetylene jet, A, was 40 mm down stream from the hydrogen jet. The reaction tube itself was 18 mm in diameter and about 25 cm long.

The detector, D, was mounted on a standard 24/40 ground joint, and could be placed at either one of two positions with the use of an extension joint. The detector wire was of platinum, from 0.0020 to 0.0025 inch in diameter and approximately 25 mm in length. It was spot-welded to nickel-tungsten lead-in wires. The nickel was shielded from contact with hydrogen by soft glass skirts, S, which reached down to the tungsten-nonex seal at the one end and at the other end were sealed to the fine platinum wire at the nickel-platinum weld. The small portion of the platinum wire covered by the soft glass did not introduce a serious error. All glass surfaces exposed to hydrogen, from the top of the tungsten filament chamber to somewhat past the detector, were given a liberal coating of metaphosphoric acid to reduce recombination on the walls.

The detector wire, its leads, and a calibrated 500 ma meter formed one arm of a Wheatstone bridge; the other three arms consisted of a 1000 ohm Leeds and Northrup standard resistance and two decade boxes. A G.M. table galvanometer with a sensitivity of approximately 0.4 micro ampere per mm served as the null detector. The bridge current was supplied by a storage battery and could be varied by means of a rheostat.

Considerable time was devoted to a study of the characteristics of the detector before doing any experiments with acetylene. With the tungsten filament off, but with hydrogen flowing through the system at the desired pressure, the bridge current was adjusted until the resistance of the detector wire corresponded to the desired temperature, say 400°C. Allowance was made for the resistance of the meter and leads. When the tungsten filament was turned on, the temperature of the detector wire would increase due to the recombination of atomic hydrogen on its surface. The bridge current was then lowered until the bridge was again in balance. With the detector wire again at 400°C, heat losses thereby being eliminated, the *decrease* in the wattage supplied to the detector is a measure of the number of hydrogen atoms recombining on its surface per second.

If the recombination coefficient is assumed to be unity[7] the number of hydrogen atoms striking a unit area per second can be calculated in terms of the wattage decrease, W_H. It is equal to

$$\frac{2\times 6.023\times 10^{23}\times W_H}{4.183\times 103{,}680\times A},$$

where A is the area of the wire in cm². The area of the wire was determined at the end of each series of experiments by cutting it off closely, measuring its length, and weighing it on a micro balance. From the kinetic theory expression for the number of particles striking a unit area per second it was then possible to calculate the

[7] W. V. Smith, J. Chem. Phys. 11, 110 (1943).

pressure of atomic hydrogen, P_H. The resulting equation is:

$$P_H = 1.483 \times 10^{-3} W_H/A \text{ mm.} \quad \text{(a)}$$

It was assumed that the average velocity of the hydrogen atoms striking the detector wire was determined by the temperature of the walls of the reaction tube. Experiments using nitrogen instead of hydrogen showed that no heat was carried from the tungsten filament to the detector.

The commercial electrolytic hydrogen used in this work was purified continuously by passing it over hot platinized asbestos and then through a trap cooled with liquid air, before admitting it to the reaction system. Acetylene was freed from acetone and other impurities by passing it through two traps cooled with a mixture of dry ice and acetone and then subjecting it to a series of bulb-to-bulb distillations. The middle fraction was stored in a two liter bulb. No impurities could be detected by analysis.

In carrying out an experiment using acetylene a sample was transferred from the storage bulb to a calibrated gas burette. The volume of the gas in the burette was adjusted by a mercury piston to give a pressure somewhat less than atmospheric. This pressure was read on a U tube manometer having an electrical contact in the vacuum arm. As the acetylene left the burette and entered the reaction vessel through an orifice the electrical contact in the manometer operated a relay which caused a current to pass through a solution of sodium sulphate in an electrolysis cell. The hydrogen and oxygen produced raised the mercury piston and kept the pressure in the burette constant to within a fraction of a mm. The gases issuing from the reaction tube passed through several traps cooled with liquid air; the liquid air around the last trap was pumped continuously, reducing its temperature to a point where all gases except methane and hydrogen would be frozen out. It would seem highly unlikely that any methane would be produced in this reaction. The hydrogen was pumped off through a mercury diffusion pump and a Pressovac pump; it could be either collected and measured over a pneumatic trough or passed into a fume duct. The steady-state pressure in the system was adjusted by two Hoke high vacuum valves (No. 318), one on each side of the reactor.

At the end of an experiment all residual hydrogen was pumped off and the traps warmed to room temperature. The gases were condensed into a bulb at the bottom of a second gas burette. After isolating this burette from the rest of the system, the liquid air was removed and the gas compressed into the calibrated portion by raising a mercury levelling bulb. After measuring its volume and pressure it was transferred, by means of a Toepler pump, to one of the small test tubes used with the Blacet-Leighton gas analysis apparatus. In later experiments a large part of the unreacted acetylene was first removed by a preliminary treatment with alkaline mercuric iodide under vacuum conditions. In the actual analyses acetylene was removed with alkaline mercuric cyanide beads.[8] Ethylene was determined by the hydroxy mercurial method,[9] paraffins by combustion.[8]

EXPERIMENTAL RESULTS

Production and Determination of Atomic Hydrogen

The effect of the temperature of the detector wire on the wattage developed by recombination was investigated over a temperature range of approximately 125°C to 460°C, for various pressures of hydrogen. The whole range could not be covered at a single hydrogen pressure, since to heat the detector to 460°C under a high pressure of hydrogen would require a current in excess of the capacity of the bridge. A large number of experiments were made, of which the two recorded in Table I are typical. The resistance of the detector wire, R, is given rather than its temperature. Correction was made for the resistance of the leads and the meter. The limiting value of R at low currents was 1.33 ohms. W_H was calculated from the expression

$$W_H = R(I_0^2 - I_H^2), \quad \text{(b)}$$

where I_0 and I_H are the detector currents in the absence and in the presence of atomic hydrogen.

[8] F. E. Blacet, A. L. Sellers and W. J. Blaedel, Ind. Eng. Chem. (Anal. Ed.) **12**, 356 (1940).
[9] R. Pyke, A. Kahn and D. J. Le Roy, Ind. Eng. Chem. (Anal. Ed.) **19**, 65 (1947).

It is clear from these experiments that W_H is independent of the temperature of the detector wire over quite a wide range; this is not proof, however, that W_H is a true measure of the pressure of atomic hydrogen. Experiments in which purified nitrogen was used instead of hydrogen showed no change in R when the tungsten filament was turned on, showing that the effect was not due to hot gas. Two additional experimental tests were applied, one to study the effect of the temperature of the tungsten filament on W_H, the other to study the effect of hydrogen pressure.

If it can be assumed that thermodynamic equilibrium is obtained at the tungsten filament, and that this equilibrium is "frozen" until the gas reaches the detector, then the decrease in standard free energy for the reaction $H_2=2H$ is given by

$$-\Delta F^\circ = RT \ln P_H^2/P_{H_2}, \qquad (c)$$

where P_H is the pressure of atomic hydrogen at the detector, P_{H_2} is the pressure of molecular hydrogen, R is the gas constant and T is the absolute temperature of the tungsten filament. P_{H_2} is so close to the total pressure that the difference can be neglected. If the total pressure is kept constant, and if the standard heat of formation of atomic hydrogen is approximately independent of temperature over the range, there should be a linear relationship between the logarithm of P_H and the reciprocal of the absolute temperature of the tungsten filament; the slope should be given by the expression:

$$d \log P_H/d(1/T) = d \log W_H/d(1/T) = -\Delta H^0/(4.606R). \qquad (d)$$

The results of two sets of experiments, done several months apart, are shown in Fig. 2. Different detector wires and hydrogen pressures were used in the two cases and hence the intercepts of the two curves would not be expected to be the same. The values of ΔH^0 obtained from the lower and upper curves are 76 and 89 kcal., respectively, the latter value being the more recent.

A more definitive test was made by computing the equilibrium constant, K_p, for the reaction $H_2=2H$ at a fixed tungsten temperature of 1700°C. The data are given in Table II. Giauque[10] obtained a value of 3×10^{-6} for K_p at 1727°C. In view of the uncertainty in our value of the temperature the agreement is probably as good as can be expected.

The Catalytic Effect of Acetylene on the Recombination of Atomic Hydrogen

The effect on the concentration of atomic hydrogen of the addition of small quantities of acetylene is shown in Table III. The total pressure in the reaction tube, essentially the pressure of molecular hydrogen, is given in column one. The acetylene pressures in column three were calculated from the measured flow rate of hydrogen and the rate at which the acetylene left the first burette. The reaction time

TABLE I. Effect of detector temperature on W_H.*

Hydrogen pressure = 0.547 mm. Flow rate** = 25 cc/min. Distance, filament-detector = 75 mm.				Hydrogen pressure = 8.56 mm. Flow rate—330 cc/min. Distance, filament-detector = 115 mm.			
I_0 amps.	I_H amps.	R ohms	W_H watts	I_0 amps.	I_H amps.	R ohms	W_H watts
0.269	0.213	3.237	0.0875	0.498	0.337	2.627	0.354
0.259	0.200	3.096	0.0839	0.477	0.296	2.421	0.339
0.249	0.180	2.894	0.0857	0.455	0.228	2.259	0.350
0.239	0.154	2.672	0.0892	0.434	0.168	2.146	0.344
0.229	0.134	2.404	0.0828	0.424	0.129	2.093	0.341
0.220	0.099	2.186	0.0844	0.415	0.042	2.020	0.345
0.215	0.091	2.112	0.0800	0.405	0.000	1.996	0.336
0.210	0.068	2.039	0.0805				
			0.0843±3%				0.344±1.5%

* Tungsten filament temperature = 1650±50°C; R = 1.33 ohms at 25°C.
** Flow rates are expressed as cc of hydrogen, measured at 25°C and one atmosphere pressure, per minute.

[10] W. F. Giauque, J. Am. Chem. Soc. 52, 4808 (1930).

given in the fourth column is the time required for the reactants to pass from the acetylene jet to the detector. At the beginning of an experiment the apparatus would be run for some time before adding the acetylene. This served to establish a constant flow rate of hydrogen and to "burn up" any impurities on the detector. The final steady value of the wattage due to recombination on the detector is given in column five. The values found after adding acetylene to the gas stream are given in column six. Pseudo-first order rate constants were calculated from the expression

$$\ln(W_H^0/W_H)=\ln([H]_0/[H])=k[C_2H_2]\tau. \quad (e)$$

The values of k are given in the last column of Table III. Despite the fluctuations in k it is clearly independent of the pressure of molecular hydrogen. It would appear that the rate equation for the removal of atomic hydrogen is of the form

$$-d[H]/dt=k[H][C_2H_2]. \quad (f)$$

It should be noted, however, that the range of acetylene pressures used was not large.

The Formation of Products

All attempts to detect products other than hydrogen and acetylene under the conditions of Table III were unsuccessful. However, condensible products were found when the acetylene pressure was increased to a value sufficient to reduce the pressure of atomic hydrogen at the detector to zero. Reaction times of as much as 0.28 seconds were used but in no case was the percentage of products greater than about $\frac{1}{2}$ percent, based on acetylene. Increasing the temperature of the reaction tube to 100°C had little effect. Although the analyses were subject to considerable experimental error, evidence was found for the presence of both an olefin and a paraffin. The latter appeared to be ethane. Experiments performed with the tungsten filament at room temperature showed no measurable amount of impurity in the original gases. In general the amount of acetylene recovered agreed with the amount introduced within two percent.

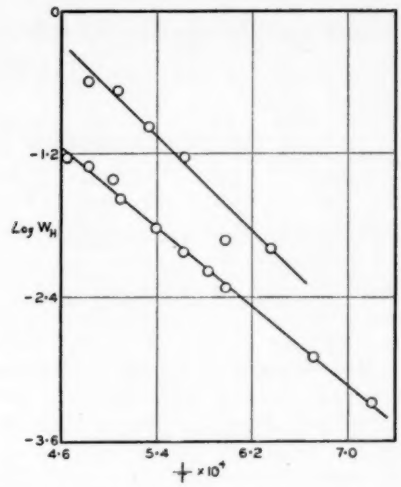


FIG. 2. The effect of the temperature of the tungsten filament on the logarithm of the wattage produced by recombination of the atomic hydrogen on the platinum detector. The upper and lower curves correspond to heats of recombination of 89 and 76 kcal., respectively.

DISCUSSION

The results given in Table III can be interpreted on the basis of either Mechanism I or Mechanism II. It has not been pointed out previously that reactions (1) and (2) alone, or (3) and (4) alone, do not fulfill the requirement that the ultimate products be stable. For example, if (3) and (4) were the only reactions occuring the concentration of ethynyl radicals would build up to a maximum and remain at that value indefinitely. The maximum value would be given by

$$d[C_2H]/dt=k_3[H][C_2H_2]-k_4[H][C_2H]=0,$$

or

$$[C_2H]_{max}=(k_3/k_4)[C_2H_2]. \quad (g)$$

Some reaction consuming ethynyl radicals would have to occur even if no products could be detected. This might be reaction (7) or (8),

$$2C_2H=C_4H_2. \quad (8)$$

The analogous reactions for Mechanism I would be (5), (6), (9) or (10),

$$2C_2H_3=C_4H_6, \quad (9)$$

$$2C_2H_3=C_2H_2+C_2H_4. \quad (10)$$

Some evidence for (10) has been found in another

TABLE II. Apparent equilibrium constant for the reaction $H_2=2H$.*

Pressure mm	W_H watts	P_H mm $\times 10^3$	K_p mm $\times 10^6$	Flow rate cc/min.
1.15	0.149	4.62	18.5	40
5.64	.194	6.02	6.41	200
8.75	.234	7.25	6.02	360
12.9	.283	8.77	5.97	460

* Tungsten filament temperature $=1700\pm50°C$; distance, tungsten filament to detector $=73$ mm.

TABLE III. Recombination of atomic hydrogen in the presence of acetylene.*

Pressure mm	Distance jet-detector mm	C_2H_2 mm $\times 10^3$	τ sec.	W_H^0 watts	W_H watts	k molec.$^{-1}$ cm^3 sec.$^{-1}$
1.00	52	1.41	0.0246	0.0727	0.0620	1.42×10^{-13}
3.62	52	1.47	0.0250	0.0732	0.0539	2.68
6.14	52	1.61	0.0231	0.0680	0.0507	2.44
10.80	52	1.35	0.0220	0.0641	0.0553	1.53
1.98	52	1.68	0.0307	0.0953	0.0789	1.13
1.02	110	1.86	0.0447	0.0916	0.0560	1.83
4.59	110	2.38	0.0555	0.0675	0.0394	1.26
9.36	110	2.10	0.0519	0.0647	0.0368	1.60
14.60	110	1.81	0.0496	0.0620	0.0403	1.48
						1.71 ± 0.4

* Reaction tube at room temperature; tungsten filament temperature $=1650\pm50°C$; cross section of reaction tube $=2.26$ cm^2.

connection.[11] To avoid confusion it will be assumed that Mechanism II obtains; any conclusions drawn can be expressed in terms of Mechanism I if the need should arise.

Unless atomic hydrogen is regenerated in some way its rate of decay will be determined by reactions (3) and (4), and at any time, t, its concentration will lie within the limits,

$$\ln[H]_0-k_3[C_2H_2]t>\ln[H]>\ln[H]_0-2k_3[C_2H_2]t. \quad \text{(h)}$$

If (3) were faster than (4) the upper limit of (h) would be approached, the concentration of ethynyl radicals would become quite appreciable, and a considerable amount of product would be expected. For this reason we believe that the rate constant, k, of Table III is probably very close to $2k_3$($2k_1$ for Mechanism I).

It is concluded that at 25°C the rate constant of the rate-determining step for the recombination of atomic hydrogen catalyzed by acetylene is $\frac{1}{2}k$, or 8.6×10^{-14} molecules^{-1} cm^3 sec.$^{-1}$. It has been customary in work of this type to express experimental results in terms of an activation energy, even when the data are confined to a single temperature. Although such a procedure is admittedly dangerous, the values obtained may be of some use in comparing data from various sources. The usual value assigned to the steric factor is 0.1. An estimate of 2.72A for the mean collision diameter was obtained from Sponer's values for the C−C and C−H bond distances in acetylene[12] and Bonhoeffer and Harteck's value of 2.14A for the diameter of the H atom.[13] The value of the activation energy of reaction (3) (or (1)) computed in this way is 3.9 kcal. per mole.

Considerable work remains to be done on this reaction. Not only is it impossible to distinguish between the two mechanisms, but the range of experimental conditions which we have been able to use does not eliminate the possibility that the catalytic recombination may be at least partially heterogeneous. It should also be noted that the concentration of atomic hydrogen was determined at only one point in the reaction vessel during an experiment and hence no correction could be made for possible recombination on the wall, even in the absence of acetylene.

The authors wish to express their thanks to the Advisory Committee on Scientific Research of the University of Toronto for a grant which supported this research.

[11] J. W. Hodgins, A. W. Tickner, and D. J. Le Roy, in press.

[12] A. Farkas and H. W. Melville, *Experimental Methods in Gas Reactions* (MacMillan and Company, Ltd., London, 1939).

[13] K. F. Bonhoeffer and P. Harteck, *Photochemie* (Steinkopff, Leipzig, 1933).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

The Vibrational Spectra of Molecules and Complex Ions in Crystals. I. General Theory*

DONALD F. HORNIG
Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island

(Received May 24, 1948)

It is shown that if a crystal is approximated as a harmonic oscillator, only a very small number of vibrational modes may be active in the infra-red or Raman spectra. These modes are all totally symmetric with respect to translation. They must also have proper symmetry with respect to the factor group of the space group which we have called the unit cell group. The active frequencies may be calculated from a single unit cell. It is shown further that the number and symmetry type of vibrational modes may be correctly calculated from the local symmetry (site group) of the center of gravity of each kind of molecule. In the harmonic approximation the spectrum should consist of very sharp lines. The wide bands obtained experimentally are probably due to combination lines with lattice vibrations and indicate anharmonic coupling between molecular and lattice modes. Such combinations may cause apparent violations of selection rules for internal vibrations. The symmetry basis for obtaining selection rules in this case is given. The importance of obtaining spectra over a wide temperature range and particularly at very low temperatures is emphasized. In cases where all internal modes have a frequency great compared to the frequency of lattice modes the problem is examined from the point of view of the Born-Oppenheimer approximation. It is shown that for some symmetries perturbations linear in the lattice displacement may occur. In these cases considerable splitting of degenerate molecular vibration modes is possible. Groups for which first-order splitting is not expected are listed. Symmetry species of other groups are classified into those which may and which may not be split in this approximation, and the lattice modes responsible for splitting are classified as rotations or translations and by symmetry type.

I. INTRODUCTION

THE molecules of a crystal, unlike those of a gas, have a relatively fixed orientation in space. If the structure of the crystal is known from x-ray data, the use of polarized radiation in infra-red or Raman investigations aids enormously in making vibrational assignments. On the other hand, if the vibrational assignments of the free molecule are known, it may be possible to use the spectroscopic data to indicate crystal structure, particularly in hydrogen containing compounds for which it is exceedingly difficult to obtain x-ray data. It may also be possible to obtain data regarding the crystalline field.

Unfortunately, the spectra obtained from molecular crystals are complicated and their interpretation has not been clear. It has been known for a long time that the vibration frequencies of molecules in crystals are not very different from the corresponding frequencies in the gaseous state. When the problem is examined in greater detail, however, a number of significant differences appear. There is a great change in the shape of the envelope or the nature of the fine structure of vibration bands. Degenerate vibrations are split, even in cases such as calcite, where the equilibrium crystal symmetry as well as the ion symmetry is consistent with degeneracy. Both degenerate vibrations are split by about 50 cm^{-1} in this case. Finally, selection rules are altered and apparently "forbidden" transitions appear.

This problem has been discussed by a number of authors, but it seems desirable to develop the problem of the dynamics of molecules in crystals systematically, with particular emphasis on their rigorous basis in symmetry. We shall give a quite general discussion of the crystal in the harmonic oscillator approximation, noting that the predicted spectra are very simple. We shall conclude that the harmonic approximation is inadequate to account for important experimental effects. Since the coupling between molecules in a crystal is usually weak compared to the intramolecular forces, we shall introduce a general crystalline field as a perturbation and examine the more important consequences. These arise chiefly through anharmonic coupling between lattice modes of the crystal and internal modes of vibration of the molecules.

* The work reported here was supported in part by the Office of Naval Research under Contract N6ori-88, Task 1.

II. SYMMETRY PROPERTIES

Let us consider the symmetry properties of a crystal which we shall assume to be infinite. The theory of space groups[1,2] shows that a lattice structure must have the symmetry of one of the 230 space groups. The space group of a crystal is that group (in a mathematical sense) of operations which carries each atom into an identical atom. These symmetry operations include the translations which generate the lattice plus the symmetry operations familiar in point groups. The unit cell is the smallest unit in which no atoms are equivalent under simple translations. However, some of them may, in general, be equivalent under any of the other symmetry operations. The crystal lattice is constructed from the unit cell by the translations which carry any unit cell into any other. Similarly, the complete set of symmetry elements of the crystal is obtained from those of the unit cell by these same translations. The choice of unit cell is not unique but this makes no difference in the following discussion.

The space group is then an infinite group. However, if we define the translations which carry a point in a unit cell into the equivalent point in another cell as identity, we define a finite group which is a factor group of the space group.[2] With our convention regarding translations, this group describes the symmetry of a unit cell, and we shall call it the *unit cell group*. In general, it is *not* a point group although the possible factor groups are isomorphous with the 32 point groups which may occur in crystallography.

If we define the operations of the unit cell group as (U), those of the infinite group of translations by (T), and those of the space group by (S), we can then write:

$$(S)=(U)\times(T). \tag{1}$$

It is a theorem of group theory that irreducible representations of a factor group, (U), are also irreducible representations of the entire group, (S). In these particular irreducible representations the elements of the invariant subgroup, (T), are all given by identity. Furthermore, these are the only irreducible representations having this property. Consequently, the set of irreducible representations of (S) which are totally symmetric with respect to translation are given by

$$\Gamma^S\equiv\Gamma^U. \tag{2}$$

No simple structure can be assigned to the infinity of remaining irreducible representations, but in the detail to which we shall go we will find them unnecessary.**

It is possible to simplify still further. About any point in the crystal, there is a local symmetry which, for most points, will consist only of the identity operation, E. If, however, the point in question is located on one or more symmetry elements, the corresponding operations leave that point invariant. The symmetry operations belonging to the elements passing through the point form a *point group* which describes the symmetry of the crystal viewed from the point in question. Following the nomenclature of Halford[3] we shall call this group which describes the local symmetry a site group. A point of given local symmetry may be invariant or have one, two, or three degrees of freedom, depending on whether it lies at the intersection of two or more elements (not both planes), on an axis, on a plane, or on no symmetry elements. Since the remaining symmetry operations of the space group (or unit cell group) carry the point into an equivalent point (which has, therefore, the same local symmetry about it), there is a definite number of equivalent points of each type. A convenient table giving all of the possible local symmetries (site groups) of each type for any space group, together with the number of equivalent points of each symmetry, has been given by P. Niggli[4] and more recently by Halford[3] who does not, however, distinguish between points of the various types. These site groups are the *subgroups* of the unit cell group or,

[1] A. Schoenflies, *Krystallsysteme und Krystallstruktur* (B. F. Teubner, Leipzig, 1891).

[2] W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1945). The theory of space groups is concisely presented in Chapter 2.

** *Note added in proof.* The author has been informed by Mr. H. Winston and Professor R. S. Halford that they will discuss the irreducible representations of space groups in detail in a forthcoming publication.

[3] R. S. Halford, J. Chem. Phys. **14**, 8 (1946).

[4] P. Niggli, *Geometrische Kristallographie des Diskontinuums* (Gebrüder Bornstraeger, Leipzig, 1919), Table IV, pp. 404–411.

alternatively, factor groups of the subgroups of the space group.

Consequently, all of the operations of the unit cell group may be obtained by taking all possible products of operations contained in the site groups, noting, of course, that any operation which carries a point into the equivalent point in another unit cell must be treated as identity. It is always possible to write linear relations between the irreducible representations of the unit cell group and those of any site group. Irreducible representations which are so related may be called corresponding irreducible representations. The correspondence may be determined in any specific case by comparing the character tables of the site group and the unit cell group. (The character table of the unit cell group can always be obtained from that of the isomorphous point group containing the same subgroups.) In this way, correlation charts can be set up between the various site groups and the unit cell group. These relations are discussed analytically in Section III. Bethe[5] has described the correlation between spherical symmetry and the local symmetries which may occur in crystals, and Mulliken[6] has discussed the correlations between the point groups in some detail.

To illustrate these ideas, let us examine the space group D_{3d}^6, which describes the crystals of calcite and α-Al_2O_3. From Niggli we find that the unit cell contains two equivalent points of symmetry D_3, two of symmetry $C_{3i}(S_6)$, and six of symmetry $C_i(S_2)$. These points are fixed uniquely. In addition, it contains an infinite number of sets of four equivalent points of symmetry C_3, which are arbitrary in that one member of each set may be selected at any point on the C_3 axis (i.e., it has one degree of freedom), and sets of six equivalent points of symmetry C_2, one of which is any point on a C_2 axis. Finally, it contains sets of twelve points about which there is no symmetry at all. The character tables for these possible local symmetry groups are as follows:

D_3	E	$2C_3$	$3C_2'$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

C_{3i}	E	C_3	C_3^2	i	S_6	S_6^5
A_g	1	1	1	1	1	1
A_u	1	1	1	−1	−1	−1
E_g	1	ω	ω^2	1	ω	ω^2
	1	ω^2	ω	1	ω^2	ω
E_u	1	ω	ω^2	−1	$-\omega$	$-\omega^2$
	1	ω^2	ω	−1	$-\omega^2$	$-\omega$

C_3	E	C_3	C_3^2
A	1	1	1
E	1	ω	ω^2
	1	ω^2	ω

C_i	E	i
A_g	1	1
A_u	1	−1

C_2	E	C_2
A	1	1
B	1	−1

In these tables $\omega = \exp(2\pi i/3)$.

The possible elements of D_{3d}^6 are obtained by taking all of the possible products between elements of the subgroups, noting, of course, that the points about which the point symmetries are taken are not coincident in space, and that lattice translation is regarded as identity. It is not necessary to consider any groups which are subgroups of other groups, so that only D_3 and C_{3i} need be considered. In this case, the only unusual operation is $C_2 \cdot i$ where the axis and center of symmetry do not coincide. In crystallography this element is called a glide plane and the corresponding operation σ_v (glide). Table I the character table for the unit cell group of D_{3d}^6.

TABLE I.

	E	$2C_{3i}(2S_6)$	$2C_3$	i	$3C_2 \cdot i$	$3C_2$
A_{1g}	1	1	1	1	1	1
A_{1u}	1	−1	1	−1	−1	1
A_{2g}	1	1	1	1	−1	−1
A_{2u}	1	−1	1	−1	1	−1
E_g	2	−1	−1	2	0	0
E_u	2	1	−1	−2	0	0

The group D_{3d}^6 has the same character table and is isomorphous with the point group D_{3d}. The correlations between the irreducible representations of the various site groups and the unit cell group are given in Table II. (When two lines originate at the same E it is only pseudodegenerate and is composed of two nondegenerate irreducible representations whose characters form complex conjugate pairs.)

A few very general statements about the transformation of certain quantities by a translation will suffice for our purposes. Since translation leaves any vector invariant, it is necessarily true that, in addition to vectors, dot and cross products of vectors as well as rotations are invariant. Furthermore, all orders of derivatives are invariant under translation.

[5] H. Bethe, Ann. d. Physik **3**, 133 (1929).
[6] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

Now we shall be interested in matrix elements of the form

$$m_{ij}=\int \psi_i^* \mathbf{M} \psi_j d\tau, \tag{3}$$

where $\mathbf{M}$ is any operator and, in particular, the Hamiltonian operator $\mathbf{H}$, the dipole moment operator $\mathfrak{y}$, or the polarizability tensor $\mathbf{P}$, and the ψ's are suitable wave functions for the system. Such an integral can exist only if the reducible representation of its integrand contains the totally symmetric representation of the space group. From Eq. (2) we can then write for any of the specific operators mentioned

$$\Gamma^S(\mathbf{M}) \equiv \Gamma^U(\mathbf{M}). \tag{4}$$

Consequently, we require that

$$\Gamma^S(\psi_i^*)\Gamma^U(\mathbf{M})\Gamma^S(\psi_j) \text{ contains } A_1{}^S, \tag{5}$$

where $A_1{}^S$ is the totally symmetric representation of the space group. This then demands that

$$\Gamma^U(\mathbf{M}) \text{ contains } \Gamma^S(\psi_i^*)\Gamma^S(\psi_j) \tag{6}$$

since the product of two irreducible representations cannot be totally symmetric unless they are identical (or complex conjugates). In particular, such integrals can always exist in the special case where

$$\Gamma^U(\mathbf{M}) \text{ contains } \Gamma^U(\psi_i^*)\Gamma^U(\psi_j). \tag{7}$$

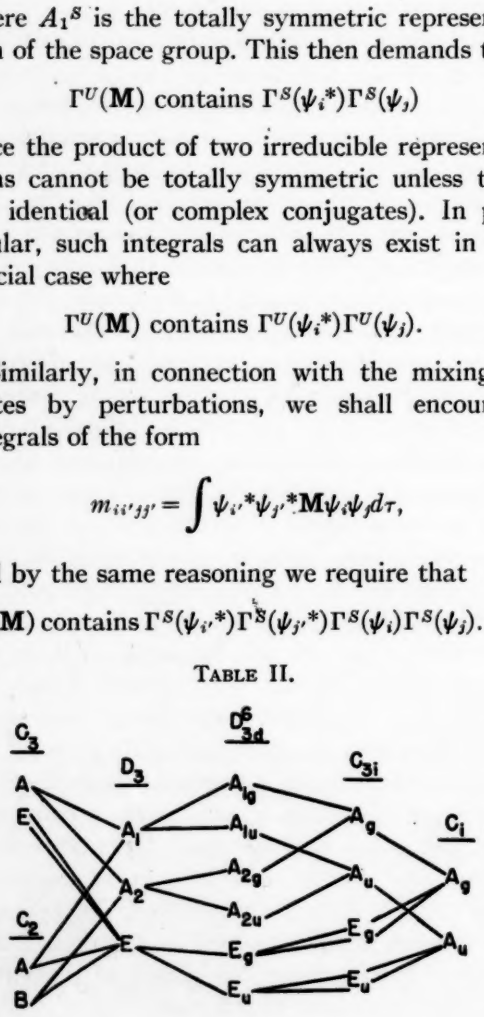
Similarly, in connection with the mixing of states by perturbations, we shall encounter integrals of the form

$$m_{ii'jj'}=\int \psi_{i'}^* \psi_{j'}^* \mathbf{M} \psi_i \psi_j d\tau, \tag{8}$$

and by the same reasoning we require that

$$\Gamma^U(\mathbf{M}) \text{ contains } \Gamma^S(\psi_{i'}^*)\Gamma^S(\psi_{j'}^*)\Gamma^S(\psi_i)\Gamma^S(\psi_j). \tag{9}$$

TABLE II.



Such integrals may always exist in the special case where

$\Gamma^U(\mathbf{M})$ contains

$$\Gamma^U(\psi_{i'}^*)\Gamma^U(\psi_{j'}^*)\Gamma^U(\psi_i)\Gamma^U(\psi_j). \tag{10}$$

III. THE HARMONIC APPROXIMATION

If the potential function for the system includes only quadratic terms, it is known from the theory of small vibrations that it is possible to find coordinates (which are linear combinations of the original coordinates) such that the kinetic and potential energy can be put in the form

$$2T=\sum_i \dot{Q}_i^2, \tag{11}$$

$$2V=\sum_i \omega_i^2 Q_i^2. \tag{12}$$

In this case the motion of the system can be resolved into the motions of a set of independent harmonic oscillators of angular frequency ω_i in the normal coordinates Q_i. The wave function for the crystal is then

$$\phi=\prod_i \psi_{ni}(Q_i) \tag{13}$$

when the functions, ψ_{ni}, are given explicitly by

$$\psi_{ni}(Q_i)=\exp[-(\pi\omega_i/h)Q_i^2] \times H_{ni}[(2\pi\omega_i/h)^{\frac{1}{2}}Q_i], \tag{14}$$

where H_{ni} is the Hermite polynomial of degree n. The energy levels in the harmonic approximation are given by

$$E=\sum_i (n_i+\tfrac{1}{2})h\nu_i, \tag{15}$$

where

$$2\pi\nu_i=\omega_i.$$

If the Hamiltonian, H, and hence T and V, are to be invariant under all of the operations of the space group of the crystal, the coordinates Q_i must transform as the irreducible representations of the group. The functions H_{ni} are odd or even functions of Q_i according to whether n_i is odd or even. If Q_i belongs to a non-degenerate irreducible representation, the corresponding ψ_{ni} transforms either as Q_i or the totally symmetric representation according as n_i is odd or even.

The selection rules in either the infra-red or Raman spectra are given, respectively, by the

non-vanishing of the components of the integrals

$$m_{n'n}=\int \psi_{n'i} \mathbf{v} \psi_{ni} dQ_i,$$

and (16)

$$P_{n'n}=\int \psi_{n'i} \mathbf{P} \psi_{ni} dQ_i.$$

The situation is the same in this respect as in free molecules except that the distinction between the components, e.g., μ_x, μ_y, and μ_z, has physical significance. Hence, the selection rules may be different for different orientations of the crystal and different polarization of the radiation.

As is customary in vibrational theory, we shall consider only linear terms in the expansion of $\mathbf{v}$ and $\mathbf{P}$. In that case such integrals can exist in the harmonic approximation only if $\Delta n_i = \pm 1$, and the observed frequency is the same for all values of n. From Eq. (4) we know that $\mathbf{v}$ and $\mathbf{P}$ have components only in the normal coordinates belonging to those irreducible representations of S which are also irreducible representations of U. Since the integrals of Eq. (16) involve only one normal coordinate, they can exist only for normal coordinates whose symmetry type is some $\Gamma_k{}^U$. That is, only those normal coordinates of the crystal which are totally symmetric with respect to translation may be active, and then only if the transition is allowed under U. The selection rules for fundamentals are thus given exactly by Eq. (7).

Explicitly, we may write any totally symmetric coordinate of the crystal in the form

$$Q_i{}^S(\Gamma_k{}^S)=\sum_{m=1}^{N} [Q_i{}^U(\Gamma_k{}^U)]_m, \qquad (17)$$

where the sum is over all the unit cells and the coordinate in brackets might be called a normal coordinate of the unit cell. Physically, this motion is that in which equivalent atoms of all unit cells are in phase. Such modes are relatively easy to compute and have been used as an approximation.[7] We see that this approach is rigorous for the calculation of observed fundamental modes.

An immediate consequence of this one-to-one correspondence between the irreducible representations of the unit cell group and those irreducible representations of the complete space group which can be active as fundamentals in either the infra-red or Raman spectrum is the rule: *in the harmonic approximation the total number and symmetry type of the observed frequencies in either the Raman or infra-red spectrum must be equal to the number and symmetry type determined by the molecules in a single unit cell.*

Since the number of atoms in a unit cell is finite and, in most cases of interest, small, we conclude that if the harmonic approximation is adequate, the infra-red and Raman spectra should consist of a few very sharp lines of breadth equal to the natural line breadth. This follows since we have already included all of the degrees of freedom of the system in our discussion and there are no others (such as rotational degrees of freedom in the gas phase) to couple with a vibration to yield a band rather than a line.

In the simple case of cubic crystals, such as NaCl and MgO, we should then expect a single sharp line in the infra-red spectrum. Absorption measurements on these materials[8,9] at room temperatures, as well as on a large number of other cubic crystals by other investigators have shown bands more than 100 cm^{-1} wide (1000 cm^{-1} in the case of MgO) with a great deal of fine structure. This has already been ascribed by the authors to anharmonic coupling between normal modes and discussed theoretically by Born and Blackman[10] and by Seitz.[9]

However, we can go much further than this. A considerable line breadth is found in all infra-red spectra of crystals,[11] and in the relatively few cases which have been examined under high resolution such as, for example, NH_4Cl and NH_4Br[12] and the 7μ band of calcite,[13] a wealth of fine structure is evident. Similarly, diffuse fundamentals are frequently found in the Raman spectra although, in general, the Raman lines are much sharper than the corresponding lines

[7] S. Bhagavantam and T. Venkatarayadu, Proc. Ind. Acad. Sci. A9, 224 (1939).

[8] R. B. Barnes and M. Czerny, Zeits. f. Physik 72, 447 (1931).

[9] R. B. Barnes, R. R. Brattain, and F. Seitz, Phys. Rev. 48, 582 (1935).

[10] M. Born and M. Blackman, Zeits. f. Physik 82, 551 (1933); M. Blackman, Zeits. f. Physik 86, 421 (1933).

[11] See, for instance, C. Schaeffer and F. Matossi, *Das Ultrarote Spektrum* (Verlag-Julius Springer, Berlin, 1930).

[12] C. Beck, J. Chem. Phys. 12, 71 (1944).

[13] S. Silverman, Phys. Rev. 39, 72 (1932).

in the infra-red spectrum. We conclude that the available data points to the inadequacy of the harmonic approximation.

Nevertheless, we should like to develop it a little further as a basis for higher approximations. It has been pointed out by Halford[3] that the local symmetries may be used to determine selection rules if the molecules other than the one considered are kept in their equilibrium position. Let us investigate the relation between the rigorous (in harmonic approximation) selection rules obtained under the unit cell group and those obtained using the local symmetries.

Suppose that the reducible representation of a physical property C, such as any of the components of μ or P, has been put in the form

$$\Gamma^U(C)=\sum_k c_k{}^U\Gamma_k{}^U. \tag{18}$$

Then, from Eqs. (7) and (16), this property may be observed with those frequencies, ν_i, whose corresponding normal coordinate, Q_i, belongs to an irreducible representation, $\Gamma_i{}^U$, for which $c_i{}^U$ is not zero. If we now represent the irreducible representations of U, considered as vectors whose components are the corresponding characters $\chi_k{}^U(R)$, in terms of the irreducible representations, $\Gamma_i{}^r$, of the rth site group L^r, we write

$$\Gamma_k{}^U=\sum_i b_{ki}{}^r\Gamma_i{}^r, \tag{19}$$

where

$$b_k{}^{ir}=(1/h^r)\Gamma_k{}^U\cdot\Gamma_i{}^r=\sum_R\chi_k{}^U(R)\chi_i{}^r(R)/h^r. \tag{20}$$

This is just an analytical statement of the correlation chart. The $b_{ki}{}^r$ are non-vanishing when a line connects $\Gamma_i{}^r$ and $\Gamma_k{}^U$. Since this transformation will have applied to the normal coordinate and the physical property, they will both transform as any $\Gamma_i{}^r$ for which $b_{ki}{}^r\neq 0$ and hence would be predicted to be active under L^r. That is, every normal coordinate which may be active under the unit cell group must also be active under any of the local symmetry groups.

Let us now examine the converse situation. Suppose that we consider the crystal from the point of view of Halford.[3] Then we divide the atoms of the crystal among molecules M^r, with local symmetry L^r. From this point of view we consider that all molecules, M^r, of a symmetrically equivalent set have the same frequencies, so that in order to count frequencies we need consider only a single molecule of each set. If a reducible representation of a molecule, M^r, is $\Gamma^r(M^r)$, the number of distinct frequencies, $n_i{}^r$, occurring in $\Gamma_i{}^r$ is given by

$$n_i{}^r=(1/h^r)\Gamma^r(M^r)\cdot\Gamma_i{}^r, \tag{21}$$

where h^r is the order of L^r. These frequencies may be active in the infra-red or Raman spectrum, respectively, if the reducible representation of $\boldsymbol{\nu}$ or $\mathbf{P}$ contains $\Gamma_i{}^r$. According to Halford the selection rules for the crystal are obtained if Eq. (21) is written for each symmetrically non-equivalent kind of molecule.

A difficulty arises in applying these selection rules to the separate components of $\boldsymbol{\nu}$ or $\mathbf{P}$ as we should like to do when considering polarized radiation. The reason is that if the x, y, and z coordinates are fixed in space (and hence in the crystal), the various symmetrically equivalent molecules, M^r, of a given set are not, in general, similarly oriented with respect to these axes. Consequently, although Eq. (21) will be shown to yield the proper number of active frequencies in either the infra-red or Raman spectrum, it must be modified if the selection rules with regard to the separate components of $\boldsymbol{\nu}$ and $\mathbf{P}$ are to be obtained when the components are designated by space-fixed axes.

This is readily done if we remember that the reference axes of the groups U and S are fixed in space. Suppose that according to Eq. (18) a given component of $\boldsymbol{\nu}$ or $\mathbf{P}$ transforms as $\Gamma_k{}^U$. The number of times each $\Gamma_i{}^r$ occurs in $\Gamma_k{}^U$ is given by Eq. (19). Using Eq. (21) we then find that the total number of distinct frequencies occurring in $\Gamma_k{}^U$ (and which are therefore active and have the polarization of the given component of $\boldsymbol{\nu}$ or $\mathbf{P}$) resulting from molecules of type M^r is

$$(n_k{}^U)^r=\sum_i n_i{}^r b_{ki}{}^r.$$

The selection rules in this form are plainly equivalent to those expressed in Eq. (21). In the first case the reducible representation of $\boldsymbol{\nu}$ or $\mathbf{P}$ is reduced directly into the irreducible representations of L^r while in the second the same reduction is effected in two steps. The total number of distinct frequencies occurring in $\Gamma_k{}^U$ due to all molecules is then, from the

Halford point of view,

$$n_k{}^U = \sum_r \sum_i n_i{}^r b_{ki}{}^r. \tag{22}$$

We shall now show that, in the harmonic approximation, these selection rules are correct. We make no assumptions whatever about the degree to which the motions of the molecules are coupled. It has previously been shown that the selection rules for the crystal may be obtained from the unit cell group and the molecules within a single unit cell. The unit cell must contain h^U/h^r molecules of type M^r since there are h^U/h^r equivalent site groups, L^r (conjugate subgroups). We shall formally designate this set of symmetrically equivalent molecules by

$$((h^U/h^r)M^r).$$

A reducible representation of the entire unit cell may be designated by

$$\Gamma^U(\sum_r (h^U/h^r)M^r).$$

The number of distinct frequencies, $n_k{}^U$, occurring in some $\Gamma_k{}^U$ is

$$n_k{}^U = (1/h^U)\Gamma^U(\sum_r (h^U/h^r)M^r)\cdot\Gamma_k{}^U. \tag{23}$$

Since none of the sets with different r are symmetrically equivalent, we can write

$$\Gamma^U(\sum_r (h^U/h^r)M^r) = \sum_r \Gamma^U((h^U/h^r)M^r). \tag{24}$$

Furthermore, the character of any transformation of a set of symmetrically equivalent molecules, $((h^U/h^r)M^r)$, is zero if the transformation is not included in L^r, since all such operations interchange members of the set (i.e., any operation of U which leaves the center of gravity of a molecule, M^r, invariant implies a corresponding symmetry element passing through the center of gravity. The operations of such elements are included in L^r by definition). Noting the definition of a dot product given in Eq. (20), we have

$$\Gamma^U((h^U/h^r)M^r)\cdot\Gamma_k{}^U = (h^U/h^r)\Gamma^r(M^r)\cdot\sum_i b_{ki}{}^r\Gamma_i{}^r. \tag{25}$$

Equation (23) then becomes, after substituting Eqs. (24) and (25)

$$n_k{}^U = \sum_r \sum_i n_i{}^r b_{ki}{}^r. \tag{26}$$

This is just the expression obtained in Eq. (22) by considering isolated molecules with the appropriate local symmetry. We had previously noted that the total number of frequencies active in either the infra-red or Raman spectrum must be the same whether computed from Eq. (21) as in Halford's paper or from Eq. (22). We can now state the following conclusion which is generally valid in the harmonic approximation; *the number of frequencies active in either the infra-red or Raman spectrum calculated from the local symmetries of the molecules* (including each non-equivalent type of molecule once) *is exactly equal to the number calculated on the basis of the unit cell, which is equal to the allowed number for the entire crystal.* It is not possible to calculate the polarization properties from local symmetry alone, but using the coefficients $b_{ki}{}^r$ they can be obtained from Eq. (26).

Since the group L^r is a subgroup of U, an irreducible representation of U cannot contain an irreducible representation of L^r of higher degeneracy. Consequently, no degenerate vibration obtained in the local symmetry approach can ever be split when the entire crystal is considered. However, we have previously pointed out that several irreducible representations of U may contain the same irreducible representation of L^r. They differ physically in the phase in which equivalent molecules are coupled. If the polarizability occurs in $\Gamma_k{}^U$, the dipole moment occurs in $\Gamma_l{}^U$, and both $b_{ki}{}^r$ and $b_{li}{}^r$ exist, then a mode which was active in both the infra-red and Raman spectra under $\Gamma_i{}^r$ might appear with different frequencies in the two spectra when the entire unit cell is considered. The difference in frequency is a measure of the effect of coupling between molecules.

In order to see the problem more explicitly, let us designate the displacement of the center of gravity of each ion or molecule as well as the displacement of the angles which define the orientation of a set of axes fixed to each molecule (with respect to axes fixed in the entire crystal) by the coordinates $s_{ij}{}^r$. Here the superscript refers to the kind of molecule and the subscripts to the specific molecule and coordinate (e.g., the ith coordinate of the jth molecule of the rth kind). These coordinates we shall call lattice coordinates, and they are analogous to the

coordinates which define the translation and rotation of a free molecule. Six of them are required to describe each non-linear ion or molecule (five of them are required in the linear case and three for a monatomic ion).

Let us describe the distortion of the configuration, relative to the center of gravity and body axes, of the rth kind of molecule by the internal coordinates, $m_{ij}{}^r$. These are internal coordinates in the same sense as in the usual molecular vibration problems. There are then $3n-6$ internal coordinates describing a non-linear molecule or ion containing n atoms. We may use an equivalent set of coordinates, both lattice and internal, for every symmetrically equivalent molecule of a given kind.

In these coordinates, the potential energy is given in the harmonic oscillator approximation by the expression

$$V=\sum R_{jj'ii'}{}^{rr'}s_{ji}{}^r s_{j'i'}{}^{r'}+\sum M_{ii'}{}^r m_{ji}{}^r m_{ji'}{}^r$$
$$+\sum K_{ji'ii'}{}^{rr'}m_{ji}{}^r m_{j'i'}{}^{r'}+\sum L_{jj'ii'}{}^{rr'}m_{ji}{}^r s_{j'i'}{}^{r'}$$
$$=V_s+\sum_r\sum_j V_j{}^r+V_{mm'}+V_{ms}. \quad (27)$$

The first term is the potential function of the lattice if there is no interaction with the internal vibrations of the molecules (or, alternatively, if the molecules are considered rigid bodies). The second term is the sum of the potential functions, $V_j{}^r$, for the internal motion of the individual molecules when there is no interaction between the internal motions of the various molecules nor between the internal motions and the lattice vibrations. The remaining terms are small; the third represents the coupling of the internal modes of different molecules, and the fourth represents interaction between lattice and internal vibrations.

In terms of these same coordinates, the kinetic energy is of the form

$$T=\sum A_j(\dot{s}_{ji}{}^r)^2+\sum B_{ii'}\dot{m}_{ji}{}^r\dot{m}_{ji'}{}^r+\sum C_{ii'}\dot{m}_{ji}{}^r\dot{s}_{ji'}{}^r$$
$$=\sum_r\sum_j[T_{sj}{}^r+T_{mj}{}^r+T_{msj}{}^r], \quad (28)$$

where $\dot{s}_{ji}{}^r$ and $\dot{m}_{ji}{}^r$ are the velocities corresponding to $s_{ji}{}^r$ and $m_{ji}{}^r$ and the coefficients are functions of the coordinates and masses. The first term is the translational and rotational energy of the molecules considered as rigid bodies, the second is the internal kinetic energy of the molecules and is analogous to that encountered in any molecular vibration problem, and the third represents the interaction between the internal angular momentum of each molecule and the overall angular momentum. Hence, only three of the six coordinates, s, of each molecule appear in this term.

It is apparent empirically that the interaction terms, $V_{mm'}$ and V_{ms}, are small. If they were neglected entirely the problem would be separable, both classically and quantum-mechanically, into the problems of the lattice vibrations and the individual molecules. The lattice vibration problem may be handled by methods developed by Born, Blackman, and others.[14] We shall not pursue it in detail except to note some general behavior. It is convenient to replace the original translations and rotations, $s_{ij}{}^r$, of a given molecule by linear combinations, $q_i{}^r(\Gamma_k{}^r)$, which transform as irreducible representations of L^r. In the case of these lattice coordinates the interaction terms with the lattice coordinates of other molecules are strong, so that these coordinates are not even approximately normal coordinates. Using the correlation chart between L^r and U, or Eq. (20), we can form h^U/h^r orthogonal linear combinations from the equivalent coordinates, $q_i{}^r(\Gamma_k{}^r)$, of the h^U/h^r symmetrically equivalent molecules having symmetry L^r. These coordinates are symmetry coordinates of the unit cell group and transform as some $\Gamma_j{}^U$. We shall denote them by $q_i{}^U(\Gamma_j{}^U)$. If the original set of coordinates was orthogonal, there is no ambiguity in this procedure, even in the case of degenerate representations.

We have previously shown that the lattice modes which are active in the infra-red and Raman spectra are totally symmetric with respect to translation. The sum over all unit cells of $q_i{}^U(\Gamma_j{}^U)$ is a totally symmetric (translation) symmetry coordinate of the crystal and starting from those $\Gamma_j{}^U$ which may be active under the unit cell group we can immediately calculate the active normal lattice vibrations. Actually, the same calculation is made more simply by noting that in these totally symmetric modes corresponding coordinates in all unit cells are equal

[14] See, for example, M. Born, *Atomtheorie des festen Zustandes* (B. G. Teubner, Berlin, 1923).

in any coordinate system. The original kinetic and potential energies may therefore be expressed in this case in terms of the coordinates of one unit cell. The secular determinant arising with these coordinates $q_i^U(\Gamma_j^U)$ is factored as far as it can be from symmetry considerations. Its solution yields "normal coordinates of the unit cell" which are linear combinations of $q_i^U(\Gamma_k^U)$ belonging to the same irreducible representation, Γ_k^U. The frequencies are correct for the entire crystal.

If $V_{mm'}$ and V_{ms} are neglected, we must also solve the internal vibration problem once for each kind of molecule. The usual methods for a molecule whose Hamiltonian function is

$$H^r = V^r + T^r \tag{29}$$

may be used.[15] (We have omitted the subscript since the identity of the molecule is immaterial.) This problem is essentially the same as that of the free molecule except that H^r must have the local symmetry, L^r, of the molecule in the crystal. In general, this symmetry will be lower than that of the free molecule, the group L^r being a subgroup of the symmetry group of the free molecule. The solutions to this problem are a set of frequencies, ν_{ik}^r, and normal coordinates, $Q_i^r(\Gamma_k^r)$, which must transform as Γ_k^r. We have previously shown that the selection rules in terms of these coordinates are rigorous. The frequencies are very nearly correct if the neglected terms are small. In the absence of specific intramolecular coupling such as hydrogen bonding this approximation is quite satisfactory.

As a matter of fact, since T^r is identical with, and V^r is only slightly different from the case of a free molecule, even these frequencies will usually be very nearly the same as those in the free molecule, although degeneracies may be split. Similarly, although selection rules are relaxed by the lowered symmetry, the new frequencies need not appear with appreciable intensity. If the normal coordinates and the corresponding frequencies of the free molecule are known, the change in frequencies may be calculated by the usual perturbation methods.

From the sets of equivalent $Q_i^r(\Gamma_k^r)$ of molecules in a single unit cell we can, following Eq. (20), construct h^U/h^r orthogonal symmetry coordinates, $S_j^U(\Gamma_k^U)$, of the unit cell. In the limit of vanishing interaction terms these are true "normal coordinates" of the unit cell. If the cross terms are included, rewritten in terms of the coordinates $S_j^U(\Gamma_k^U)$ and $q_i^U(\Gamma_k^U)$, they will consist only of products of coordinates of the same species, Γ_k^U. The exact normal coordinates will then contain small admixtures of other symmetry coordinates of the same species. Nevertheless, because the coupling is weak the normal modes of the unit cell will still be divided into a set whose frequency is very nearly the same as the $Q_i^r(\Gamma_k^r)$ which we shall continue to call internal modes, and a low frequency set whose frequencies are nearly those of the $q_i^U(\Gamma_k^U)$ which we shall still term lattice modes.

The normal coordinates of the unit cell have frequencies identical with those modes of the entire crystal which are totally symmetrical with respect to translation (and which may be observed in the infra-red or Raman spectra). The calculation of the other crystal modes (which are inactive, however, as fundamentals in either the infra-red or Raman spectrum) is enormously difficult. Because of the weakness of the interactions we may anticipate that all of the high frequency crystal modes arising from a single internal mode will lie within a fairly narrow frequency range.

A comparison of the observed Raman spectrum with that expected in the three cases: the hypothetical free molecule, the molecule using local symmetry, and the molecule using unit cell group symmetry, has been made by Couture[16] for single crystals containing $CO_3^=$, NO_3^-, and $SO_4^=$.

To summarize: in the harmonic approximation the spectrum of a crystal containing molecules or complex ions should consist of a small number of very sharp lines. The selection rules for those frequencies which correspond to internal modes of the molecules are obtained in this approximation by considering the individual molecules, using their actual local symmetry in the crystal. The observed frequencies may be calculated exactly by considering only one unit cell, with the aid of the unit cell group which is the factor

[15] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941); **15**, 736 (1947).

[16] L. Couture, Ann. de physique **2**, 5 (1947), ser. 12.

group of the space group obtained when all translations are considered an identity operation.

When the harmonic approximation is valid there is some advantage in the study of molecules in the crystalline state. The extreme sharpness of the lines in the spectrum would reduce the overlapping of bands as compared to the gas spectrum. The additional information which may be gained from polarization measurements, both in the Raman and infra-red spectrum, because of the fixed orientation of the molecules in space simplifies the analysis of the observed spectrum. This approximation may be expected to become increasingly valid as the temperature of the specimen is lowered, and the sharpening of the lines has indeed been observed.[17]

These advantages must, of course, be balanced against the disadvantage of reduced symmetry and the complications which are introduced by anharmonic interaction with the lattice vibrations of the crystal.

IV. THE EFFECT OF ANHARMONICITY

Just as in the case of free molecules, the effect of anharmonic terms in the potential function is to introduce overtone and combination frequencies into the spectrum. As far as the internal vibrations of the molecules in the crystal are concerned, we do not expect the situation to be particularly different from that of free molecules. An important qualitative difference may arise in the spectrum of the crystal, however, in that we may also expect combination levels to occur between internal and lattice vibrations. Since the lattice modes of most crystals are of frequency lower than 200 cm^{-1}, such combinations do not appear as separate bands, but convert the sharp line predicted in the harmonic approximation to a band which, depending on the temperature, may or may not be centered about the fundamental. Secondly, because of the enormous number of lattice modes, all of which yield combination lines in the same narrow region of the spectrum, the total intensity due to combination frequencies may be very considerable. In the case of a fundamental which is forbidden but whose combination bands with the lattice are allowed, the result may be to introduce a spectrum in the immediate vicinity of the forbidden fundamental. Such a case may occur in the doubly degenerate, 5.7-μ band of the NH_4^+ ion in NH_4Cl and NH_4Br which, although forbidden, appears with considerable intensity and a great deal of structure.

The theory of the effect of anharmonicity in crystals is identical in principle with that for free molecules.[18] If V'^s represents the anharmonic part of the potential function, we may get interaction of the two states ϕ_i^s and ϕ_j^s of the crystal if the integral

$$H_{ij}' = \int \phi_j^s V'^s \phi_i^s d\tau \tag{30}$$

exists. Since the potential, V'^s, must be totally symmetric, the product $\phi_j^s \phi_i^s$ must be so too. Consequently, both states must be of the same symmetry species with respect to the group, the unit cell group and the site groups. The symmetry discussion can always be reduced, then, to the site groups where all lattice coordinates transform as simple translations or rotations. The situation is not as simple for quantitative calculations, however, because the lattice coordinates of a given molecule are closely coupled to those of other molecules. We cannot, on that account, write any meaningful lattice wave functions for a single molecule. In Section VII we shall discuss an approach which simplifies this discussion, both mathematically and in that it provides a simple physical picture, so we shall not develop this approach further.

It is worth pointing out, however, that the symmetry properties of the states, $\psi_{ni}(\Gamma_k^s)$, which enter the ϕ's, according to Eq. (13), are not complicated in the case of internal modes, since at room temperature we are interested only in the ground state and the first excited level. However, the low frequency lattice modes may have quite complex symmetries if they are degenerate, since even at room temperature quite high values of the quantum numbers may be important. The symmetry of excited degenerate states has been given by Tisza.[19]

[17] See, for example, W. H. Avery and J. R. Morrison, J. App. Phys. **18**, 960 (1947); and R. S. Krishnan, Proc. Ind. Acad. Sci., **A26**, 932 (1947); **A27**, 321 (1948).

[18] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945).

[19] L. Tisza, Zeits. f. Physik **82**, 48 (1933).

V. SELECTION RULES FOR THE ANHARMONIC CRYSTAL

Let us consider first the selection rules involving only one normal coordinate. In the general case we can use Eq. (16), but without the restriction that $\Delta n = \pm 1$. Then from Eq. (7) we conclude that all such transitions are allowed which are allowed under (U) (or, from our previous discussion, under L^r. However, a further set may be allowed by the more general Eq. (6), but only if the transition is also allowed under U, and L^r, since the normal coordinates under any Γ^s may be written as a linear combination of Q_i^U. Consequently, the selection rules may be determined from U alone, but instead of a sharp line we may expect a band. In particular, since all first overtones are allowed in the Raman spectrum, we expect that they may be diffuse.

In the case of combination bands in which changes in two quantum numbers may occur, the selection rules depend on the non-vanishing of the integrals

$$m = \int \psi_{i'} \psi_{j'} \mathfrak{y} \psi_i \psi_j d\tau \tag{31}$$

or

$$P = \int \psi_{i'} \psi_{j'} \mathbf{P} \psi_i \psi_j d\tau. \tag{32}$$

The most important cases are certainly those for which $i' = i \pm 1$ and $j' = j \pm 1$. Just as before, we can say that if these transitions are to occur, they must be allowed under U, and L^r, according to Eq. (10). If they are allowed under U, they may also be allowed under Eq. (9), in which case the line will be broadened into a band. In the case in which ψ_i and ψ_j both refer to internal vibrations, these transitions give rise to the usual combination bands. If ψ_i refers to an internal vibration and ψ_j refers to a lattice vibration, these transitions have the effect of adding structure to the simple transition in ψ_i if it is allowed, or of producing an apparent violation of selection rules if the simple transition is forbidden. The situation is complicated, of course, because at room temperature the crystal is not normally in a ground state as regards lattice vibrations but may be in a rather high level. Consequently, a multiplicity of lines may be expected due to anharmonicity.

We can proceed similarly for higher combinations, and the number of allowed frequencies increases rapidly, but in the absence of more empirical information, it would be of little value to go further.

VI. THE EFFECT OF TEMPERATURE

If a crystal is studied at sufficiently low temperatures, both the lattice and molecules may be regarded as in their ground state. The infra-red or Raman spectrum obtained under these circumstances is as simple as it can be for the crystal since all anharmonic effects are minimized. If they make no contribution, each line should be exceedingly sharp and the selection rules derived from the harmonic approximation should be valid. Even if anharmonicity is present, difference bands are not allowed, so that all combination bands must appear on the high frequency shoulder of the fundamental.

As the temperature is raised, we may expect the molecules to remain largely in the ground state. The population of upper lattice states will increase. Consequently, difference bands will appear on the low frequency shoulder and at sufficiently high temperatures the band should become symmetrical. Because of the increasing effect of anharmonicity as high lattice modes are excited, we may expect the line width to increase further and the intensity of the combination lines to rise.

Secondly, forbidden lines may appear. The intensity of such lines may be expected to increase as the temperature is raised. The existence of a line whose total intensity depends strongly on temperature would argue for large anharmonic terms, since in the harmonic approximation the intensity should be independent of temperature. This effect may make it possible to identify "forbidden" lines.

It seems probable that the study of the temperature dependence of spectra will be of critical importance in the elucidation of crystal dynamics.

VII. ANOTHER POINT OF VIEW

We should like to reduce the discussion of the effect of lattice vibrations on the internal modes of a molecular crystal to a discussion involving only individual molecules, in the same fashion as

we found possible in the harmonic approximation. This was not possible from the point of view of ordinary anharmonic theory. The reason is that although the problem could easily be set up in terms of the vibrational wave functions of individual molecules, $\psi_{ni}{}^{r}$ (since internal modes are very weakly coupled), the lattice wave functions involve coordinates throughout the crystal and are not conveniently discussed from a local point of view except as regards their symmetry properties.

That some of the interaction, at least, can be treated from a local point of view seems apparent physically in the following way. If the frequency of all lattice vibrations is sufficiently low compared to the frequency of the internal vibrations of the molecules, the lattice coordinates may be considered to be essentially constant during several cycles of the internal motion. However, the lattice coordinates would affect this motion in that they would determine the symmetry and quantitative magnitude of the potential field in which the molecular vibration takes place. In particular, when all lattice coordinates have the value zero, the crystal is in its equilibrium configuration and the symmetry of the Hamiltonian of each molecule (H^{r}) is L^{r}. For any other value of the lattice coordinates, this symmetry will, in general, be lowered. In many cases, this effect may be visualized qualitatively. If we imagine, for example, a tetrahedral molecule such as NH_4^+ at the center of a cubic unit cell with the N−H bonds directed along threefold axes of the cube toward four cube corners, the local symmetry of the NH_4^+ ion (if similarly oriented in *all* unit cells) is T_d. Such a crystal possesses only two types of translational lattice modes, those in which the motion of the ions at the corners of the cube is parallel to that of the NH_4^+ ion and those in which it is antiparallel. The first mode is triply degenerate and is equivalent to a translation of the entire unit cell. Depending on the relative phase of the motion in different unit cells, it gives rise to the various *acoustical modes* of vibration of the crystal. Particularly in the case of long wave-length modes of this type, we expect no perturbation of the local potential field. The other gives rise to the *optical modes* of the crystal and is observed as the Reststrahlen frequency (in the case of NH_4Cl it has a frequency of 183 cm^{-1}). This mode is also triply degenerate and it may be considered to be composed of the three vibrations perpendicular to the cube faces. If, in first approximation, these are considered separately, it is apparent that such a displacement of the center of gravity of the NH_4^+ ion reduces the symmetry from T_d to C_{2v}. In this case, both of the triply degenerate modes of the NH_4^+ ion might be expected to be split and the inactive double degenerate mode might become active. The third lattice mode is the triply degenerate torsional oscillation of NH_4^+ about the same three axes. In the same approximation, it might reduce the symmetry to C_2.

Conversely, if the frequency ratio is great, the internal vibrations would effectively be averaged so that in calculating lattice frequencies we need include only the mean molecular configuration. Since this mean configuration would, in general, vary with the lattice coordinates, the internal molecular energy (and frequencies) would be a function of these parameters. This function then constitutes a further potential energy term in the computation of lattice modes.

This type of problem was solved long ago by Born and Oppenheimer[20] for the case of electronic and nuclear motion. Their approach has been widely applied to the coupling of electronic and vibrational states in molecules.[21] A great deal of this work can be applied without change to our problem if the wave functions are appropriately renamed.

Let us write the complete potential function in the form

$$V = V_l{}^{s} + \sum_r \sum_j (V_j{}^{r} + V_{jms}{}^{r}) + V_{mm'}{}^{s} + V_{ms}{}'^{s}, \quad (33)$$

where $V_l{}^{s}$ is that part including only lattice coordinates, $V_j{}^{r}$ is that part including only internal coordinates of the jth molecule of local symmetry L^{r}, $V_{jms}{}^{r}$ includes those terms containing both internal and lattice coordinates of the jth molecule, $V_{mm'}{}^{s}$ represents (as in Eq. (27)) cross terms between internal coordinates

[20] M. Born and R. Oppenheimer, Ann. d. Physik **84**, 457 (1927). Another mathematical technique which should be applicable to this problem has recently been given by R. R. Newton and L. H. Thomas, J. Chem. Phys. **16**, 310 (1947).

[21] H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 85 (1941).

of different molecules, and $V_{ms}{}'^{s}$ represents any terms not previously included. Following our discussion of the harmonic case, we begin by ignoring the last two terms which are certainly small. The kinetic energy is given classically by Eq. (28). Since we are looking for relatively large effects, we shall also ignore the last term of Eq. (28) which is known to be small. The Schrödinger equation is then of the form

$$[\mathbf{H}_l{}^s+\sum_r\sum_j(\mathbf{H}_j{}^r+V_{jms}{}^r)-E_T{}^s]\psi_T(m,s)=0, \quad (34)$$

where the **H**'s are the corresponding Hamiltonian operators and $\psi_T{}^s(m,s)$ is the total wave function of the crystal. If all of the frequencies associated with lattice coordinates are small compared to any of the frequencies associated with internal coordinates, we may, following Born and Oppenheimer, set

$$\psi_T{}^s(m,s)=\psi_l{}^s(s)\cdot\psi_m{}^s(m,s), \quad (35)$$

where $\psi_m{}^s(m,s)$ is a solution of the equation

$$[\sum_r\sum_j(\mathbf{H}_j{}^r+V_{jms}{}^r)-E_m(s)]\psi_m{}^s(m,s)=0, \quad (36)$$

in which the lattice coordinates, s, are regarded as parameters, and $\psi_l{}^s(s)$ is a solution of the equation

$$[\mathbf{H}_l(s)+E_m(s)-E_T{}^s]\psi_l{}^s(s)=0. \quad (37)$$

Since Eq. (36) is separable, we have also

$$E_m(s)=\sum_r\sum_j E_{jm}{}^r(s) \quad (38)$$

$$\psi_m{}^s(m,s)=\prod_{r,j}\psi_{jm}{}^r(m,s) \quad (39)$$

$$[\mathbf{H}_j{}^r+V_{jms}{}^r-E_{jm}(s)]\psi_{jm}{}^r(m,s)=0. \quad (40)$$

If the functions $\psi_l{}^s(s)$ and $\psi_m{}^s(m,s)$ are degenerate, Eq. (35) must be replaced by a linear combination of similar terms.

This is discussed by Born and Oppenheimer and by Sponer and Teller. The quantitative validity of this approximation will be discussed at a later date. If the frequency ratio is very great, it is certainly quite valid, but in cases in which some of the internal molecular modes are of very low frequency, it is certainly not applicable. Even in these cases, a similar approach can still be used in discussing the perturbation of the high frequency molecular modes.

We are particularly interested in the solutions of Eq. (40) which yield the molecular energy levels (and frequencies) as a function of the lattice coordinates. We need solve this equation only once for each type of molecule present so that we will omit the subscript j. The quantity H^r may be taken to be identical with that in Eq. (29) since, for our purposes, the harmonic approximation is adequate for the internal vibrations. The quantity $V_{ms}{}^r$ is in the nature of a perturbation, and we shall take it to include harmonic coupling terms as well as anharmonic terms of any functional form whatever, subject only to the general symmetry restriction that it must have the symmetry properties of the group L^r.

We shall use as the basis functions for a perturbation treatment the functions $\psi_{ns}[Q_i(\Gamma_k{}^r)]$ which we shall designate hereafter simply as $\psi_{nik}{}^r(m)$. These functions are solutions of the equation

$$(\mathbf{H}^r-E_{nik}{}^r)\psi_{nik}{}^r(m)=0, \quad (41)$$

and have the form given by Eq. (14) if the coordinates $Q_i(\Gamma_k{}^r)$ are the normal coordinates of the unperturbed molecule. The corresponding frequencies are just those of the local symmetry approximation which we have previously discussed.

According to the usual methods of perturbation theory a state $\psi_{nik}{}^r(m)$ may be perturbed by those states $\psi_{n'i'k'}{}^r(m)$ for which the integrals

$$H'=\int\psi_{nik}{}^r(m)\,V_{ms}{}^r\psi_{n'i'k'}{}^r(m)d\tau(m) \quad (42)$$

exist. In the case of small amplitude lattice

TABLE III. The splitting of degenerate molecular vibrations by crystal lattice vibrations.

Site group	Irreducible representation	Lattice mode responsible for splitting
C_3	E	$T(E)$; $R(E)$
C_{3v}	E	$T(E)$; $R(E)$
C_{3h}	E_1', E_1''	$T(E_1')$
D_3	E	$T(E)$; $R(E)$
D_{3d}	E_g, E_u	$R(E_g)$
S_4	E	$T(B)$
$S_{4v}(D_{2d})$	E	$T(B_1)$
T	E	Not split
	F	$T(F)$, $R(F)$
T_d	E	Not split
	F_1, F_2	$T(F_2)$
T_h	E_g, E_u	Not split
	F_g, F_u	$R(F_g)$

vibrations we may expand $V_{ms}{}^{r}$ in terms of the symmetry coordinates $q_j{}^{r}(\Gamma_l{}^{r})$, which describe the rotations and translations of the molecule in question. We thus obtain

$$V_{ms}{}^{r}=\sum_j\sum_l \alpha_{jl}q_j{}^{r}(\Gamma_l{}^{r})+\cdots. \tag{43}$$

If the amplitudes are small the linear terms are most important. Equation (42) then becomes

$$H'=\sum_j\sum_l q_j{}^{r}(\Gamma_l{}^{r}) \times\int\psi_{nik}{}^{r}(m)\alpha_{jl}\psi_{n'i'k'}{}^{r}(m)d\tau(m). \tag{44}$$

The states may perturb each other if any of the integrals $\int\psi_{nik}{}^{r}\alpha_{jl}\psi_{n'i'k'}{}^{r}d\tau$ exist. Since $V_{ms}{}^{r}$ must be totally symmetric, each α_{jl} which is a function of the internal coordinates, must have the same symmetry, $\Gamma_l{}^{r}$, as $q_j{}^{r}(\Gamma_l{}^{r})$. The integrals can thus exist only if $\Gamma_k{}^{r}\Gamma_{k'}{}^{r}$ contains $\Gamma_l{}^{r}$.

The perturbation will only be important if $E_{nik}{}^{r}-E_{n'i'k'}{}^{r}$ is small and will be most important in the case of degenerate states. The perturbation will split the degenerate level in such a case. Since the symmetry of the product of the wave functions is the $(\Gamma_k{}^{r})^2$, the degeneracy may be split if $(\Gamma_k{}^{r})^2$ contains $\Gamma_l{}^{r}$. We conclude that in this approximation a degenerate mode of vibration of a molecule in a crystal may be split if the square of the symmetry species of the degenerate level contains the symmetry species of translation or rotation. We assume, however, that the molecule is stable with respect to totally symmetric lattice vibrations.

A very similar discussion has been given by Jahn and Teller[22] for the perturbation of degenerate electronic states by molecular vibrations. From their tables, it is immediately possible to predict which degenerate irreducible representations may be split. In particular, it is found that in this approximation degenerate modes of the following local symmetry groups are not split by lattice vibrations: C_4, C_{4v}, C_{4h}, D_4, D_{4h}, C_6, C_{6v}, C_{6h}, D_6, D_{6h}, O, and O_h. The symmetry types of vibrational modes which may be split are tabulated in Table III. The modes responsible for the splitting are designated T or R depending on whether they are translational or rotational in origin, and their symmetry species is indicated in parenthesis. On this basis we would predict that the degenerate vibrations of $CO_3^{=}$ in calcite, dolomite, etc., may be split. In fact, both degenerate modes are split by approximately 50 cm^{-1} (see reference 11, pp. 338 ff.). Similarly, it is predicted that the triply degenerate modes of NH_4^{+} may be split in NH_4Cl but that the doubly degenerate mode may not. This has been found to be the case, the two triply degenerate modes being split 35 cm^{-1} and 50 cm^{-1}, respectively.[23]

The only other case in which effects of considerable magnitude might occur is that in which a degenerate mode of the free molecule is slightly split by the equilibrium symmetry of the crystal. In this case the two states interact if the product of their symmetry species contains the symmetry of either rotation or translation. The consequence, in all such cases, will be to increase the separation between the two levels.

It seems fruitless to carry the discussion further at this time. The general nature of the transitions is the same as those discussed by Sponer and Teller. These same authors discuss selection rules in this approximation. It is only necessary to note that in their discussion we must substitute molecular vibrations for electronic states and lattice vibrations for molecular vibrations to make it applicable to our case.

It is even reasonable to enunciate a principle similar to the Franck-Condon principle, namely, that the position and velocity of the center of gravity of the molecules will not change during a transition between internal vibrational states. Finally, we should emphasize again the importance of temperature. The effects we have just discussed yield energy terms which are linear in the lattice vibration amplitudes. Hence, they too are minimized at low temperatures.

[22] H. A. Jahn and E. Teller, Proc. Roy. Soc. **A161**, 220 (1937).

[23] R. Pohlman, Zeits. f. Physik **79**, 394 (1932).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

Thermodynamic Functions for Tritium and Tritium Hydride. The Equilibrium of Tritium and Hydrogen with Tritium Hydride. The Dissociation of Tritium and Tritium Hydride.

W. M. JONES
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico
(Received June 10, 1948)

The heat capacity, entropy, internal energy, and free energy are calculated to 2500°C for tritium and tritium hydride. The distribution of tritium between the ortho and para states is considered. The equilibrium constant for the formation of tritium hydride from hydrogen and tritium is calculated from 50°K to 2500°K. The dissociation of tritium and tritium hydride into the atoms is discussed. The bearing of the radioactivity of tritium and tritium hydride on the attainment of thermodynamic equilibrium is briefly considered.

ACCURATE calculations of the thermodynamic properties of hydrogen have been carried out by Giauque,[1] and similar calculations have been made for deuterium and deuterium hydride by Johnston and Long.[2] The present paper presents corresponding work for tritium and tritium hydride. The values refer to a mole of the ideal gas.

The general methods of such calculations are well known. In the present calculations partition functions and their derivatives have been calculated by direct summation over rotational and vibrational states. The energies of T_2 and HT are representable in the form,

$$E_{J,\nu}=\omega_e(\nu+\tfrac{1}{2})-X_e\omega_e(\nu+\tfrac{1}{2})^2 +[B_e-\alpha_e(\nu+\tfrac{1}{2})+\gamma_e(\nu+\tfrac{1}{2})^2 +\delta_e(\nu+\tfrac{1}{2})^3]J(J+1) +[D_e+\beta_e(\nu+\tfrac{1}{2})]J^2(J+1)^2 +F_eJ^3(J+1)^3. \quad (1)$$

The constants are listed in Table I. They were computed from the data for ordinary hydrogen as given by Jeppeson,[3] who expresses the energy in a form slightly different from Eq. (1), through the theory of isotopic diatomic molecules.[4] The excellent agreement of the constants so calculated with the observations of Jeppeson[5] in the case of HD lends confidence to the present procedure. The agreement in the case of D_2[2,6] is not quite so good. It is felt that, in general, the calculations are correct to the number of significant figures given except at the highest temperatures where the large values of ν and, particularly, of J needed for the convergence of the summations lie outside the range employed by Jeppeson in fitting the constants of Eq. (1).

The constants in Table I were calculated taking the atomic weights (physical scale) of hydrogen and tritium to be 1.008130 and 3.017050.[7] The physical constants are otherwise

TABLE I. Molecular constants of T_2 and HT.

Constant	T_2 cm^{-1}	HT cm^{-1}
ω_e	3608.3	2553.8
$X_e\omega_e$	87.585	43.872
B_e	40.5747	20.3243
α_e	1.67048	0.59222
γ_e	0.030434	0.007636
$-\delta_e$	0.0024	0.00042
$-D_e$	0.02068	0.005190
β_e	0.369×10^{-3}	0.0655×10^{-3}
F_e	1.5378×10^{-5}	0.19328×10^{-5}

TABLE II. Distribution of molecular tritium among ortho and para states.

T, °K	% ortho	T, °K	% ortho
0	0.000	40	66.803
10	2.823	50	71.272
15	16.429	75	74.475
20	33.814	100	74.928
25	47.446	125	74.990
30	56.694	150	74.999
35	62.783	175	75.000

[1] Giauque, J. Am. Chem. Soc. **52**, 4826 (1930); see also C. O. Davis and H. L. Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).
[2] H. L. Johnston and E. A. Long, J. Chem. Phys. **2**, 389, 710 (1934).
[3] C. R. Jeppeson, Phys. Rev. **44**, 165 (1933).
[4] Jevons, *Report on Band Spectra of Diatomic Molecules* (Cambridge University Press, Teddington, 1932).
[5] C. R. Jeppeson, Phys. Rev. **45**, 480 (1934).
[6] C. R. Jeppeson, Phys. Rev. **49**, 797 (1937).
[7] J. Mattauch, Phys. Rev. **57**, 1155 (1940); M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 373 (1937).

TABLE III. Heat capacities and entropies (including nuclear spin) of T_2 and HT in calories per degree per mole.

T, °K	C_p^0 o-T_2	C_p^0 p-T_2	C_p^0 e-T_2	C_p^0 n-T_2	S^0 o-T_2	S^0 p-T_2	S^0 e-T_2	S^0 n-T_2	C_p^0 HT	S^0 HT
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10	4.967	4.967	6.770	4.967	18.860	14.495	14.873	18.886	4.977	16.043
15	4.967	4.981	8.970	4.971	20.874	16.510	18.115	20.901	5.142	18.083
20	4.967	5.103	8.688	5.001	22.304	17.956	20.697	22.334	5.607	19.619
25	4.967	5.447	7.743	5.087	23.414	19.126	22.535	23.460	6.195	20.934
30	4.998	5.994	7.040	5.247	24.321	20.166	23.881	24.400	6.676	22.108
35	5.055	6.609	6.630	5.444	25.095	21.136	24.933	25.222	6.972	23.162
40	5.152	7.156	6.420	5.653	25.776	22.056	25.804	25.963	7.110	24.104
50	5.458	7.989	6.390	6.091	26.956	23.732	27.220	27.268	7.141	25.698
75	6.332	7.661	6.656	6.664	29.342	26.827	29.845	29.830	7.023	28.568
100	6.784	7.145	6.874	6.874	31.237	29.001	31.795	31.795	6.987	30.582
125	6.925	7.008	6.945	6.945	32.769	30.577	33.338	33.338	6.977	32.140
150	6.958	6.975	6.963	6.963	34.035	31.851	34.607	34.607	6.974	33.412
175	6.966	6.970	6.967	6.967	35.109	32.926	35.680	35.680	6.973	34.487

T, °K	C_p^0 e-T_2	S^0 e-T_2	C_p^0 HT	S^0 HT	T, °K	C_p^0 e-T_2	S^0 e-T_2	C_p^0 HT	S^0 HT
200	6.969	36.611	6.973	35.418	700	7.345	45.439	7.096	44.183
225	6.971	37.432	6.974	36.239	800	7.510	46.430	7.181	45.136
250	6.973	38.166	6.975	36.974	900	7.674	47.325	7.285	45.987
275	6.975	38.831	6.976	37.639	1000	7.830	48.141	7.401	46.760
298.1	6.978	39.394	6.978	38.202	1250	8.166	49.926	7.708	48.445
300	6.978	39.438	6.978	38.246	1500	8.425	51.440	7.993	49.877
400	7.007	41.449	6.986	40.254	2000	8.779	53.916	8.442	52.242
500	7.077	43.019	7.002	41.815	2500	9.011	55.901	8.758	54.159
600	7.196	44.319	7.037	43.094					

those of the International Critical Tables[8] in order that these calculations may best be utilized in connection with the large body of similar calculations now existing. The experiments of Bloch, *et al.*[9] indicate the expected one-half unit of spin for the tritium nucleus.

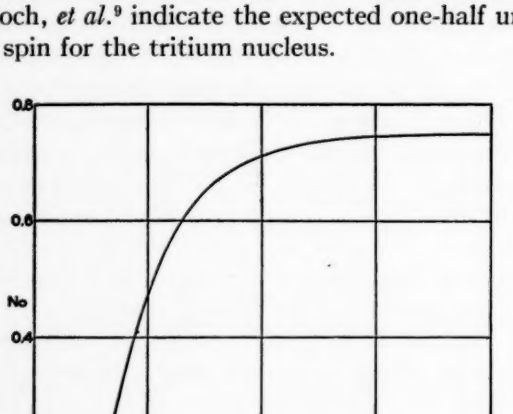


FIG. 1. Fraction of tritium molecules in odd rotational states as a function of temperature.

[8] International Critical Tables, Volume I, p. 16.
[9] Bloch, Packard, Graves, and Spence, Phys. Rev. **71**, 373(L), 551(L) (1947).

THE EQUILIBRIUM DISTRIBUTION OF MOLECULAR TRITIUM AMONG ORTHO AND PARA STATES

Like ordinary hydrogen, molecular tritium exists in ortho and para forms which occupy the odd and even rotational states, respectively, and which have the spin weights 3 and 1, respectively. The fraction of the molecules which are ortho attains the limiting value of $\frac{3}{4}$ at moderate temperatures as may be seen from Table II and from Fig. 1. The limiting value is attained at lower temperatures than is the case for hydrogen and deuterium.

It is well known that both hydrogen and deuterium gases show a very slow attainment of ortho-para equilibrium in the absence of catalysts at room temperature. It seems very likely that the radioactivity of tritium, giving rise to ionization, dissociation, and subsequent recombination, would provide an internal mechanism whereby pure tritium could attain ortho-para equilibrium at a much more rapid rate than pure hydrogen or deuterium. Rough calculations indicate that the half-time for conversion by this mechanism should be of the order of a few days.

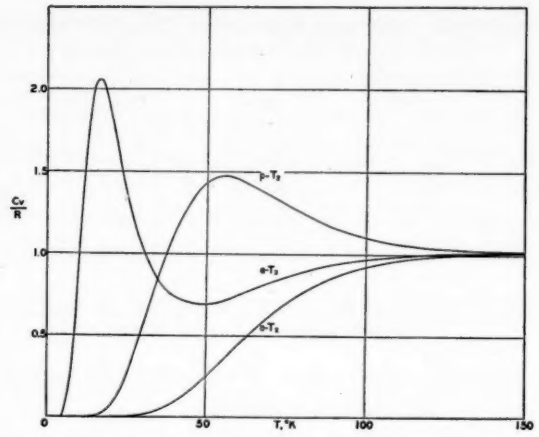


FIG. 2. Internal portion of the low temperature heat capacities at constant volume of ortho, para, and equilibrium tritium.

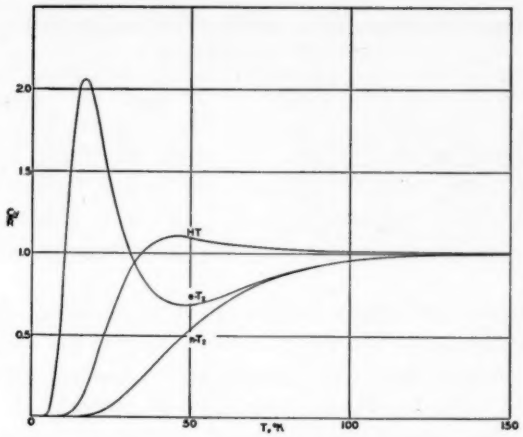


FIG. 3. Internal portion of the low temperature heat capacities at constant volume of equilibrium tritium, normal tritium, and tritium hydride.

THE HEAT CAPACITY AND ENTROPY

The heat capacities at constant pressure of ortho, para, equilibrium, and normal tritium (room temperature ortho-para distribution) are given in Table III along with the corresponding total entropies which include the nuclear spin contribution of $R \ln 4$. Values are also given for HT. By 175°K the four types of T_2 have attained identical heat capacities, and the entropies of normal and equilibrium tritium have become identical. Moreover, above this temperature, the entropies of para and of ortho tritium are less than the entropy of equilibrium or of normal tritium by very nearly $R \ln 4 = 2.754$ e.u. and $R \ln 4/3 = 0.572$ e.u., respectively. This simplifies Table III. Figures 2 and 3 show the internal portion of C_V/R at low temperatures. The characteristic features are owing to rotation.

It is well known that calorimetric measure-

TABLE IV. $E^0 - E_0^0$ in calories per degree per mole for T_2 and HT (excluding translation).

T, °K	o-T_2	p-T_2	e-T_2	n-T_2	HT
0	113.96	0.00	0.00	85.47	0.00
10	113.96	0.00	3.22	85.47	0.01
15	113.96	0.02	18.74	85.48	0.35
20	113.96	0.32	38.75	85.55	2.27
25	114.01	1.75	55.00	85.95	6.94
30	114.06	5.46	67.03	86.92	14.36
35	114.34	12.13	76.30	88.79	23.72
40	115.00	21.76	84.05	91.70	34.12
50	118.28	47.35	97.91	100.56	55.89
75	141.96	112.88	135.75	134.70	108.60
100	182.68	176.60	181.16	181.17	159.45
125	230.25	228.94	229.92	229.92	209.81
150	279.70	279.45	279.64	279.64	260.01
175	329.60	329.55	329.59	329.59	310.16
200	379.62	379.61	379.62	379.62	360.30

T, °K	T_2	HT	T, °K	T_2	HT
225	429.69	410.46	700	1436.2	1379.7
250	479.81	460.64	800	1682.3	1596.6
275	529.98	510.85	900	1944.7	1823.1
298.1	576.40	557.27	1000	2223.3	2060.5
300	580.21	561.09	1250	2983	2707
400	782.44	762.49	1500	3816	3429
500	989.5	95.0	2000	5641	5061
600	1206.1	11670.0	2500	7608	6881

TABLE V. $-[(F^0 - E_0^0)/T]$ for e-T_2, HT, and T in calories per degree per mole (spin effects included).

T, °K	e-T_2	HT	T, °K	e-T_2	HT	T
10	9.585	11.075	250	31.280	30.164	26.205
15	11.898	13.092	275	31.937	30.814	26.679
20	13.792	14.539	298.1	32.493	31.365	27.080
25	15.368	15.689	300	32.537	31.408	27.111
30	16.680	16.662	400	34.525	33.381	28.540
35	17.786	17.517	500	36.073	34.918	29.649
40	18.736	18.284	600	37.341	36.176	30.554
50	20.296	19.612	700	38.420	37.245	31.320
75	23.068	22.153	800	39.361	38.172	31.983
100	25.016	24.021	900	40.197	38.994	32.563
125	26.532	25.494	1000	40.952	39.733	33.092
150	27.775	26.711	1250	42.572	41.312	34.195
175	28.830	27.747	1500	43.928	42.623	35.106
200	29.745	28.649	2000	46.129	44.744	36.535
225	30.555	29.448	2500	47.891	46.439	37.643

TABLE VI. Equilibrium constant for $H_2 + T_2 = 2HT$.

T, °K	K	T, °K	K
50	0.242	700	3.59
100	0.947	800	3.68
200	1.948	900	3.76
298.1	2.57	1000	3.81
300	2.58	1250	3.90
400	2.99	1500	3.94
500	3.26	2000	3.98
600	3.45	2500	3.99

TABLE VII. Dissociation constants of isotopic hydrogen molecules in atmospheres.

T, °K	1000	1500	2000	2500
H_2	6.45×10^{-18}	3.60×10^{-10}	2.96×10^{-6}	6.92×10^{-4}
HD	2.48	1.57	1.36	3.28
D_2	3.71	2.70	2.49	6.17
HT	2.26	1.49	1.32	3.21
T_2	3.01	2.44	2.35	5.94

TABLE VIII. Percentage dissociation of isotopic hydrogen molecules at a total pressure of one atmosphere.

T, °K	1000	1500	2000	2500
H_2	12.7×10^{-8}	9.5×10^{-4}	8.6×10^{-2}	1.31
HD	7.9	6.3	5.8	.91
D_2	9.6	8.2	7.8	1.24
HT	7.5	6.1	5.7	.90
T_2	8.7	7.8	7.7	1.22

ments performed on H_2 in the absence of a catalyst give rise to an entropy for the gas which is lower than the computed value by $R\ln 4 + 3/4R\ln 3$. These two terms correspond to nuclear spin degeneracy and to failure of ortho-para equilibration to occur in the time of experiment, respectively. This "discrepancy" is well understood and has been considered in detail by Giauque.[1] A similar situation exists for D_2.[2,10]

Experimental determination of the entropy of tritium gas by the customary calorimetric techniques would be a difficult matter because of the fairly large amount of energy steadily being released by nuclear disintegration. Granting, however, that the calorimetric measurements could be made, we may speculate on the "discrepancy" which would exist between the calorimetric and computed entropies for T_2 gas. The term $R\ln 4$ would remain even if calorimetric measurements on solid tritium could be extended to a small fraction a degree absolute. In spite of the fact that tritium may attain ortho-para equilibrium more rapidly than hydrogen, the additional discrepancy might be a sizeable fraction of the value $3/4R\ln 3$ fully realized by hydrogen if the tritium were rapidly cooled to a low temperature and calorimetric measurements commenced.

THE INTERNAL ENERGY AND THE FREE ENERGY

The internal energy and the free energy, both given with reference to the state in which $\nu=J=0$ are given in Tables IV and V. Table IV does not include the contribution of $3/2RT$ for $(E^0-E_0{}^0)_{\text{translation}}$. The entries of Table V include the nuclear spin contribution of $R\ln 4$ for T_2 and HT and of $R\ln 4$ for atomic T, arising from the half-units of nuclear and electron spin.

[10] Clusius and Bartholomé, Zeits. physik. Chemie **B30**, 237 (1935).

THE EQUILIBRIUM OF HYDROGEN AND TRITIUM WITH TRITIUM HYDRIDE

Values of $[(F^0-E_0{}^0)/T]$ for H_2, T_2 and HT may be employed to calculate the equilibrium constant, K, for the reaction $H_2+T_2=2HT$ from the relationship:

$$-R\ln K=\Delta\left(\frac{F^0-E_0{}^0}{T}\right)+\frac{\Delta E_0{}^0}{T}. \qquad (2)$$

The values of $-[(F^0-E_0{}^0)/T]$ for H_2 were taken from the tables of Giauque[1] at 298.1°K and at higher temperatures, while the values of Urey and Rittenberg,[11] corrected to $R=1.9869$ cal. deg.$^{-1}$ mole^{-1}, were used below this temperature. The quantity $\Delta E_0{}^0$ is obtained from the zero point energies 6193.8, 3603.4, and 5072.7 cal. mole^{-1} for H_2, T_2 and HT, and it has the value 348.2 cal. mole^{-1}. The possibility of isotopic electronic shifts[2,5,6] has not been considered in this and the following section. Table VI gives values of K at several temperatures.

THE DISSOCIATION OF ISOTOPIC HYDROGEN MOLECULES

The dissociation constants of T_2 and HT have been calculated from a relationship of the form of Eq. (2). The value of $\Delta E_0{}^0$ is found from $D_0(H_2)$ and the difference in the zero point energies of H_2 and the isotopic molecule. The work of Beutler[12] provides the accurate value of $36{,}116\pm6$ cm^{-1} or $102{,}800\pm20$ cal. mole^{-1} for $D_0(H_2)$. The values for the dissociation constants of H_2, HD and D_2[1,2] are included for comparison. They need not be corrected since they were based on a value for $D_0(H_2)$ fortuitously identical to the present value. Dissociation constants are presented in Table VII. The corresponding per-

[11] H. C. Urey and D. Rittenberg, J. Chem. Phys. **1**, 137 (1933).

[12] Beutler, Zeits. Physik. Chemie **B29**, 315 (1935); Beutler and Jünger, Zeits. Physik **101**, 304 (1936).

centages of dissociation for a total pressure of one atmosphere are given in Table VIII.

The writer wishes to express his thanks for the computing assistance rendered by the following members of Dr. Bengt Carlson's computing group: Josephine Elliott, Max Goldstein, Margaret Johnson, Nell Lane, Marian Peterson, and Alice Snowden.

This paper is based on work performed at the Los Alamos Laboratory of the University of California under Government Contract W-7405-eng-36 and the information contained therein will appear in Division V of the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the Los Alamos Laboratory.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 11 NOVEMBER, 1948

Fugacity Determinations of the Products of Detonation

MELVIN A. COOK[1]
Eastern Laboratory, Explosives Department, E. I. du Pont de Nemours and Company, Gibbstown, New Jersey
(Received June 2, 1948)

By employing the equation of state derived from the hydrodynamic theory and observed detonation velocities, the thermodynamic equilibrium constant $K_p(T)$ is derived in terms of the concentrations of the various gases comprising the products of detonation and the covolume $\alpha(v)$, which may be evaluated for any known or assumed density of the products of detonation. A reiteration method is developed for solving simultaneously as many equilibria as is necessary to define completely the composition of the products of detonation. The application of the theory is illustrated by calculations for TNT which are compared with experimental data as well as results obtained from the approximate partial pressure method. Calculations are presented for several additional explosives.

THE application of the hydrodynamic theory of detonation in studies of explosives requires, in general, a knowledge of the products of detonation from which to calculate the essential thermodynamic properties, e.g., the number of moles (n) of gas produced per kilogram of explosive, the heat of explosion at constant volume (Q), the constant volume heat capacity (C_v), etc. The calculation of products of detonation in most explosives is not a simple matter, however, because the mixture may frequently consist of quite a large number of different gases interacting with each other, presumably according to the laws of thermodynamic equilibrium. It is thus necessary in an accurate treatment to solve simultaneously a series of equations involving the equilibrium constants of all of the reactions involved in determining the equilibrium mixture. The problem is further complicated by the fact that in a thermodynamically exact solution one must make use of the activity of the various components rather than the concentration or partial pressure in the thermodynamic equilibrium constants. In the particular case of gaseous explosives the activity or partial fugacity is practically equal to the partial pressure because the temperature and pressure conditions in these cases are such that the ideal equation of state,

$$pv = nRT, \tag{1}$$

applies with the required accuracy for practical applications. Lewis and Friauf[2] carried out calculations of products of detonations for some gaseous explosives taking into account the necessary equilibria, and obtained quite accurate correlations between calculated detonation velocities obtained by application of these data and experimental velocities. This work helped to demonstrate not only the validity of the hydrodynamic theory and of the ideal gas law as applied to gaseous explosives, but also that

[1] Now at the University of Utah, Salt Lake City, Utah.

[2] B. Lewis and J. B. Friauf, J. Am. Chem. Soc. **52**, 3905 (1930).

chemical equilibrium exists between the products of detonation in the detonation wave of gaseous explosives.[3]

Regarding condensed explosives, it is not valid to employ partial pressures in carrying out calculations of the equilibrium composition of the product gases because detonation pressures are thousands of times higher than in gaseous explosives. As a matter of fact, in some cases the total fugacity may be of the order of 10^4 times higher than the total pressure under the conditions occurring in the detonation wave of some high density explosives. Despite this fact, results obtained by the use of partial pressures rather than activities have been surprisingly successful in many applications of theoretical calculations.[4–6] In many cases, however, serious errors have resulted from the use of the approximation methods.

Brown[6] has developed a systematic method for taking into account as many as eleven equilibrium equations although his method employs the partial pressure approximation. Since Brown's work, the hydrodynamic theory has been worked out in considerable detail, making possible the evaluation of the equation of state applying to the product gases in detonation.[7–12]

Considerations discussed in reference (7), particularly a comparison of experimental and calculated detonation temperatures, support the assumption that an equation of state of the form

$$pv=nRT+\alpha(v)p \qquad (2)$$

applies in detonation. Here $\alpha(v)$ is a co-volume factor depending only on the specific volume, v. The present article describes the development of a method of calculation of the products of detonation, similar to Brown's method, but employing through the equation of state (2) partial fugacities instead of partial pressures in the thermodynamic equilibrium constants. The method is based on the process of reiteration in which any desired number of chemical equilibria may be taken into consideration. Fugacity calculations of the products of detonation have also been carried out by Brinkely and Wilson[9] and others, based, however, on different equations of state than (2).

TABLE I. Values of y and $e^{\Delta_{\nu}y}$ for various densities of products of detonation.*

Density	a	y	e^{y}	e^{2y}	$e^{y/2}$
0		0	1	1	1
0.5	1.089	0.95	2.59	6.69	1.62
0.60	0.829	1.22	3.39	11.47	1.84
0.70	0.633	1.52	4.57	20.9	2.14
0.80	0.5	1.85	6.36	40.5	2.53
0.90	0.396	2.22	9.21	84.8	3.03
1.00	0.32	2.67	14.44	209	3.82
1.10	0.261	3.13	22.9	524	4.81
1.20	0.216	3.65	38.5	1.48×10^3	6.23
1.30	0.179	4.20	66.7	4.45×10^3	8.17
1.40	0.153	4.79	120.3	1.45×10^4	11.02
1.50	0.130	5.39	219	4.80×10^4	14.88
1.60	0.112	6.05	425	1.81×10^5	20.7
1.70	0.095	6.78	881	7.76×10^5	29.7
1.80	0.085	7.44	1.71×10^3	2.91×10^6	41.3
1.90	0.077	8.01	3.01×10^3	9.06×10^6	55.2
2.00	0.070	8.60	5.43×10^3	2.95×10^7	73.7
2.10	0.064	9.15	9.43×10^3	8.88×10^7	97.5
2.20	0.059	9.69	1.62×10^4	2.61×10^8	127.7

* These data were calculated by Mr. R. E. Lunn, Eastern Laboratory.

THERMODYNAMIC RELATIONS

The various chemical equilibria may be expressed by the equation

$$n_1A_1+n_2A_2+\cdots\rightleftharpoons mB_1+m_2B_2+\cdots, \qquad (3)$$

where the n_iA_i refer to reactants, and the m_kB_k to products. The thermodynamic equilibrium constant may then be written in the form

$$K_p(T)=\frac{f_{A_1}{}^{n_1}f_{A_2}{}^{n_2}\cdots}{f_{B_2}{}^{m_1}f_{B_2}{}^{m_2}\cdots}=\prod_i f_i{}^{\nu_i}, \qquad (4)$$

where the Lewis[13] fugacity f is used for the activity, f_i being the partial fugacity of the ith component of the gaseous mixture, and ν_i the coefficient of this component in (3). The total fugacity is related to the pressure and specific

[3] B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases* (The Macmillan Company, New York, 1938).
[4] A. Schmidt, Zeits. ges. Schiess-Springstoffw. **29**, 259 (1934).
[5] J. Roth, Zeits. ges. Schiess-Springstoffw. **35**, 193 (1940).
[6] F. Brown, Bureau of Mines Tech. Pub. No. 632.
[7] M. A. Cook, J. Chem. Phys. **15**, 518 (1947).
[8] G. B. Kistiakowsky and E. B. Wilson, Jr., O.S.R.D. Report No. 69.
[9] S. R. Brinkley and E. B. Wilson, Jr., O.S.R.D. Reports Nos. 905, 1231, 1510, 1707.
[10] S. Paterson, Research **1**, 221 (1948).
[11] G. Morris and H. Thomas, Research **1**, 132 (1947).
[12] P. Caldirola, J. Chem. Phys. **14**, 738 (1946).
[13] G. N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances* (McGraw-Hill Book Company, Inc., New York, 1923).

TABLE II. Equilibrium constants.

K_i	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8
Reaction → / ↓ Temp. − °K	$H_2+\frac{1}{2}O_2\rightleftharpoons H_2O$	$\frac{1}{2}H_2+CH\rightleftharpoons H_2O$	$H\rightleftharpoons\frac{1}{2}H_2$	$O\rightleftharpoons\frac{1}{2}O_2$	$CO+H_2O\rightleftharpoons CO_2+H_2$	$N\rightleftharpoons\frac{1}{2}N_2$	$2NO\rightleftharpoons N_2+O_2$	$2CO\rightleftharpoons CO_2+C$
2000	7.2×10^{-6}	9.5×10^{-6}	4.4×10^{-5}	1.7×10^{-5}	4.55		4.0×10^{-4}	26
2400	8.3×10^{-5}	1.4×10^{-4}	3.9×10^{-4}	2.1×10^{-4}	5.8		0.0025	112
2800	4.7×10^{-4}	9.0×10^{-4}	1.83×10^{-3}	1.2×10^{-3}	6.6		0.0092	370
3200	1.66×10^{-3}	3.64×10^{-3}	5.80×10^{-3}	4.42×10^{-3}	7.3	7.0×10^{-5}	0.0244	815
3600	4.52×10^{-3}	1.09×10^{-2}	0.0143	0.0129	8.1	3.0×10^{-4}	0.0502	1410
4000	9.9×10^{-3}	2.54×10^{-2}	0.0292	0.0270	8.2	1.0×10^{-3}	0.100	2360
4400	0.028	0.049	0.053	0.052	8.3		0.166	3750
4800	0.082	0.075	0.083	0.087	8.55		0.247	5550
5200	0.143		0.120	0.131	8.85			
5600	0.512		0.165		9.15			

K_i	K_9	K_{10}	K_{11}	K_{12}	K_{13}	K_{14}	K_{15}	K_{16}
Reaction → / ↓ Temp. − °K	$O+2CO\rightleftharpoons 2CO_2$	$CH_4\rightleftharpoons C+2H_2$	$CH_4+H_2O\rightleftharpoons CO+3H_2$	$\frac{K_{11}}{K_5}$	K_2K_5	$(K_9K_7)^{\frac{1}{2}}$	$\frac{1}{2}N_2+\frac{3}{2}H_2\rightleftharpoons NH_3$	$HCN\rightleftharpoons C+\frac{1}{2}N_2+\frac{1}{2}H_2$
2000		0.680	0.120	0.0254	4.5×10^{-5}		32	0.0515
2400		0.324	0.018	0.003	8.3×10^{-4}	2.5×10^{-5}		0.170
2800	1.05×10^{-5}	0.192	0.005	7.3×10^{-4}	6.3×10^{-3}	3.1×10^{-4}		0.440
3200	1.66×10^{-4}				0.0350	2.0×10^{-3}		0.900
3600	0.00141				0.0905	8.6×10^{-3}		1.560
4000	0.0077				0.225	0.028	97	2.350
4400	0.104				0.406	0.132		
4800	0.470				0.641	0.327		
5200	1.60							
5600	22.00							

volume by the equation

$$nRT\left(\frac{d\ln f}{dp}\right)_T=v \tag{5}$$

which from Eq. (2) becomes

$$nRT\left(\frac{d\ln f}{dp}\right)_T=\frac{nRT}{p}+\alpha. \tag{6}$$

Integration of (6) between pressure limits of zero and p gives

$$\frac{f}{p}=\exp\frac{1}{nRT}\int_0^p\alpha dp. \tag{7}$$

The partial fugacity of the ith component is related to the total fugacity by the equation

$$f_i=fN_i, \tag{8}$$

where N_i is the mole fraction of the ith component in the mixture. Multiplying and dividing the left side of (7) by N_i and taking the ν_ith power of both sides gives

$$\left(\frac{f_i}{pN_i}\right)^{\nu_i}=\exp\frac{\nu_i}{nRT}\int_0^p\alpha dp. \tag{9}$$

Equation (4) may now be written

$$\prod_i f_i^{\nu_i}=\prod_i pN_i\exp\frac{\Delta\nu}{nRT}\int_0^p\alpha dp=K_p(T), \tag{10}$$

where

$$\Delta\nu=n_1+n_2+\cdots-m_1-m_2-\cdots. \tag{11}$$

In order to make use of Brown's developments a new form of the equilibrium constant may be defined as follows:

$$K_i=K_p\left(\frac{1.2181}{T}\right)^{\Delta\nu}. \tag{12}$$

Now

$$pN_i=\frac{N_inRT}{a}=\frac{A_i}{a}\frac{T}{1.2181}, \tag{13}$$

where $a=v-\alpha$, and A_i may be any of the A_i's or B_k's in Eq. (3) expressed in moles per 100 g of explosive while "a" has the dimensions of liters per kilogram as defined by Brown (p expressed here in atmospheres). Substituting Eqs. (12) and (13) in (10) gives

$$K_ia^{\Delta\nu}=\prod_i A_i^{\nu_i}\exp\Delta\nu y, \tag{14}$$

TABLE III. Definitions of equilibrium constants of Table II.

$K_1=((H_2)(O_2)^{\frac{1}{2}}/(H_2O))\cdot e^{v/2}/a^{\frac{1}{2}}$
$K_2=((H_2)^{\frac{1}{2}}(OH)/H_2O)\cdot e^{v/2}/a^{\frac{1}{2}}$
$K_3=((H)/(H_2)^{\frac{1}{2}})\cdot e^{v/2}/a^{\frac{1}{2}}$
$K_4=((O)/(O_2)^{\frac{1}{2}})\cdot e^{v/2}/a^{\frac{1}{2}}$
$K_5=(CO)(H_2O)/(CO_2)(H_2)$
$K_6=((N)/(N_2)^{\frac{1}{2}})\cdot e^{v/2}/a^{\frac{1}{2}}$
$K_7=(NO)^2/(O_2)(N_2)$
$K_8=(CO)\cdot e^{v}x/a$
$K_9=(O_2)\cdot e^{v}x/a$
$K_{10}=((CH_4)/(H_2)^2)\cdot a/e^{v}$
$K_{11}=((CH_4)(H_2O)/(CO)(H_2)^3)\cdot a^2/e^{2v}$
$K_{12}=K_{11}/K_5$
$K_{13}=K_2K_5$
$K_{14}=(K_9K_7)^{\frac{1}{2}}$
$K_{15}=((H_2)^{\frac{1}{2}}(N_2)^{\frac{1}{2}}/(NH_3))\cdot e^{v}/a$
$K_{16}=(HCN)/(H_2)^{\frac{1}{2}}(N_2)^{\frac{1}{2}}$

where

$$y=\frac{1}{nRT}\int_0^p \alpha dp=\int_\infty^v d\left(\frac{1}{v-\alpha}\right). \qquad (15)$$

Equation (14) differs from the approximate partial pressure equation by the factor $\exp\Delta\nu y$ which actually is unity for the most important equilibrium involved in a large number of explosives, namely, the water gas equilibrium. In many explosives, in fact, the partial pressure and fugacity methods give practically identical results for this reason.

In view of the observation discussed in reference (7), that α is the same function of v for all explosives, a conclusion which has been verified in a large number of cases involving widely different type of explosives, y (Eq. (15)) will also be the same function of v for all explosives and may be evaluated from the α *vs.* v data of Fig. 1 of reference 7. The values of y corresponding to various values of v have been evaluated by R. E. Lunn from a plot of α against $1/(v-\alpha)$ whose results are given in Table I.

Table II gives $K_i(T)$ data taken largely from Brown[6] and Schmidt,[4] although some of the data were extrapolated from curves drawn from lower temperature data and should not be regarded as entirely accurate.

METHOD OF CALCULATION

The following method of calculating the products of detonation is modeled somewhat after the method of Brown[6] which is especially convenient for use with the equation of state (2). The equilibrium constants of Table II are in a form such that one need only introduce the factor (a) as shown by Eq. (4) to convert from partial pressures to concentrations. We will consider in the present study only explosives containing carbon, oxygen, hydrogen, and nitrogen. Other types of explosives may be worked into the theory readily but, in general, it is unnecessary to do so, since when other atomic constituents are present one may generally decide what products of detonation are formed from them without taking their thermodynamic equilibria into consideration.

The atom balances of the explosive composition may be expressed as follows:

$$C_0=CO_2+CO+CH_4+HCN+2C_2N_2+\cdots, \qquad (16a)$$

$$H_0=2H_2O+2H_2+H+OH+4CH_4+HCN+3NH_3+\cdots, \qquad (16b)$$

$$N_0=2N_2+N+NO+HCN+2C_2N_2+NH_3+\cdots, \qquad (16c)$$

$$O_0=2O_2+O+NO+CO+2CO_2+H_2O+OH+\cdots. \qquad (16d)$$

Four key equations may be derived from (16) by solving for CO, H_2, N_2, and a new oxygen balance expression, giving

$$CO=B_1\left[1-\frac{CH_4+C+HCN+2C_2N_2+\cdots}{C_0}\right], \qquad (17a)$$

$$H_2=B_2\left[1-\frac{H+OH+4CH_4+HCN+3NH_3}{H_0}\right], \qquad (17b)$$

$$N_2=\frac{N_0}{2}\left[1-\frac{N+NO+HCN+NH_3+2C_2N_2}{N_0}+\cdots\right], \qquad (17c)$$

$$\Delta=-CO-H_2-\frac{H}{2}-2C-5/2HCN-4C_2N_2+4CH_4+\frac{OH}{2}+2O_2+O+NO+\cdots. \qquad (17d)$$

Here Δ is the oxygen balance,

$$B_1=\frac{C_0x}{1+x},\quad B_2=\frac{\frac{H_0}{2}x}{K_5+x},$$

and $x=CO/CO_2$. The derivatives of these functions are given by Brown. The dimensions of (a) used by Brown was liters/kg, while the atom balances were expressed in g atoms/100 g of explosive. This convention is retained here. In terms of the K_i of Table III, Eqs. (17a), (b), (c) may be written

$$CO=B_1\left(1-\frac{K_{12}(CO)(H_2)^2e^{2y}}{a^2C_0}-\frac{N_2^{\frac{1}{2}}H_2^{\frac{1}{2}}K_{16}}{C_0}-\cdots\right), \quad (18a)$$

$$H_2=B_2\left[1-\frac{a^{\frac{1}{2}}H_2^{\frac{1}{2}}\left(K_3+\frac{K_{13}}{x}\right)}{e^{y/2}H_0}-\frac{4K_{12}x(CO)(H_2)^2e^{2y}}{H_0a^2}-\frac{N_2^{\frac{1}{2}}H_2^{\frac{1}{2}}K_{17}}{H_0}-\cdots\right], \quad (18b)$$

$$N_2=\frac{N_0}{2}\left[1-\frac{N_2^{\frac{1}{2}}a^{\frac{1}{2}}K_6}{N_0e^{y/2}}-\frac{a^{\frac{1}{2}}N_2^{\frac{1}{2}}K_{15}}{xN_0e^{y/2}}-\frac{N_2^{\frac{1}{2}}H_2^{\frac{1}{2}}K_{17}}{N_0}\right]. \quad (18c)$$

The values of (a) and $e^{\Delta vy}$ may be determined from the conditions under which the computations are to be made, i.e., the known or assumed density. One may then proceed as follows:

Step I. A trial temperature is taken. It is convenient first to estimate this temperature from some approximate calculation, e.g., by writing approximate chemical equations for the explosive reaction, or one may make a rough calculation assuming only the water gas equilibrium (K_5) to be important.

Step II. Find the value of x (by a process of successive approximations) by means of Eqs. (18a), (b), (c) together with whatever auxiliary equilibrium equations (see Table III) are needed to make a complete set, such that Eq. (17d) gives the same value of Δ as the equation

$$\Delta=O_0-2C_0-\frac{H_0}{2}. \quad (19)$$

Step III. When the value of x is found such that Eqs. (17d) and (19) give identical results for the oxygen balance, one may compute from the composition obtained the heat of explosion Q and the average heat capacity $\bar{C}_v$ between T_0 and T which will then allow one to derive T for adiabatic explosion, by the equation

$$T=Q/\bar{C}_v+T_0 \quad (20)$$

or, when dealing with the detonation wave conditions, by the Eq. (16), reference 7, namely,

$$T_2=(Q+T_1\bar{C}_v)\beta/(\beta\bar{C}_v-\tfrac{1}{2}nR). \quad (21)$$

Step IV. Repeat steps II and III until the temperature calculated from (20) or (21) agrees with that used in the computations in step II.

In case of large oxygen deficiency, the method of calculation may conveniently be altered to take into account the relative importance of the coke oven equilibrium, (K_8). The selection of a particular x then immediately fixes the values of both CO and CO_2. The remaining C_0 may be then distributed: (a) as CH_4 which may be computed from Eq. (7), Table III; (b) the carbon remaining may be considered to go into HCN until Eq. (16), Table III, is satisfied; (c) any C_0

TABLE IV. Products of detonation of TNT from theoretical fugacity and partial pressure methods, and Haid and Schmidt's experimental method.

	A. "Explosion" state		Exp. Haid and Schmidt	B. "Detonation" wave state	
I. ρ=1.59 g/cc products	fugacity method	partial pressure		fugacity method	partial pressure method
CO (moles/kg)	9.4	15.9	9.39	1.7	15.5
CO_2	6.8	3.2	5.47	9.7	3.4
H_2	0.6	2.9	1.63	0.07	2.7
H_2O	3.4	4.3	6.09	3.1	4.2
N_2	5.0	5.2	—	4.4	4.0
CH_4	2.2	1.25	0.42	1.1	0.7
NH_3	1.1	0.13	1.5	3.4	0.1
HCN	2.0	2.65	0.32	1.0	5.3
Carbon	10.4	7.8	14.6	16.3	5.9
n (moles gas/kg)	30.5	35.6		24.5	35.8
Q	1120	860		1105	770
$\bar{C}_v$	0.342	0.317		0.338	0.326
T_2	3420	2975		4150 (T_2)	3300 (T_2)
II. ρ=1.0 g/cc					
CO	16.8	18.2	17.0	16.3	23.1
CO_2	3.5	2.0	2.84	2.8	0.9
H_2	2.5	4.3	2.49	1.5	4.4
H_2O	2.6	3.2	3.77	4.5	1.3
N_2	5.5	5.7	4.75	4.6	5.1
CH_4	1.9	1.2	0.1	2.3	1.8
NH_3	0.8	0.1	2.85	0.7	0.2
HCN	1.4	1.72	0.47	3.2	2.9
Carbon	7.1	7.3	10.0	5.9	2.1
n (moles gas/kg)	35.1	36.6		35.9	39.7
Q	865	780		870	660
$\bar{C}_v$	0.317	0.304		0.332	0.303
T_2	3000	2830		3340 (T_2)	2280

TABLE V. Explosion properties of various types by fugacity and partial pressure methods. (a = fugacity method; b = partial pressure method.)

Products	PETN (density = 1.6) (a)	(b)	Cyclonite (1.6) (a)	(b)	LNG (1.6) (a)	(b)	Tetryl (1.6) (a)	(b)	60% St. Dyn. (1.32) (a)	(b)
CO (moles/kg)	4.7	6.5	8.0	10.1	1.1	2.6	10.6	18.1	6.7	7.0
CO_2	11.1	9.3	5.5	3.4	12.1	10.6	6.6	2.9	8.3	8.0
H_2	0.5	0.9	1.3	3.5	0.1	0.3	0.5	2.9	0.9	1.1
H_2O	10.9	11.2	8.0	9.8	10.8	10.2	2.2	4.0	10.0	10.1
N_2	5.9	6.1	12.1	13.5	6.4	6.0	7.0	7.0	4.9	4.9
OH	0.1	0.6	—	0.3	0.2	0.9	—	—	—	0.1
NO	0.1	0.5	—	—	0.5	1.2	—	—	0.01	0.02
O_2	—	0.2	—	—	1.4	1.4	—	—	—	—
Na_2O	—	—	—	—	—	—	—	—	1.11	1.11
SO_2	—	—	—	—	—	—	—	—	—	—
CaO	—	—	—	—	—	—	—	—	0.16	0.16
CH_4	—	—	—	—	—	—	1.6	0.1	—	—
NH_3	0.8	—	2.8	—	—	—	0.9	—	0.3	—
HCN	—	—	—	—	—	—	2.9	3.4	—	—
C	—	—	—	—	—	—	2.7	—	—	—
n	34.1	35.4	37.7	40.7	32.6	33.3	32.3	38.3	31.1	32.3
Q	1420	1310	1315	1250	1420	1240	1013	910	985	975
T_3	4770	4420	4530	4330	4780	4350	3650	3470	3690	3590

remaining may be considered to go to free carbon. This calculation is necessarily approximate in view of the absence of heat data for other possible products of detonation involving carbon.

RESULTS

Table IV presents calculated results for TNT at densities of 1.59 g/cc (cast) and 1.0 g/cc for (*A*) "adiabatic" or "explosion" conditions, and (*B*) for conditions occurring at the Chapman-Jouguet plane. Also included in Table IV are experimental results obtained by Haid and Schmidt[14] in a method designed to "freeze" the equilibrium corresponding to the "explosion" state. A careful examination of the comparative results between experimental and calculated data reveals some definite consistencies if one interprets the experimental data on the basis that the experimental method does not entirely "freeze" the equilibria at those corresponding to "explosion" state. The excellent agreement in CO is probably not fortuitous; this type of agreement is quite general as has been found in numerous other comparisons by the author of calculated and experimental data. In fact, one has theoretical justification for the consideration that a moderate shift in the water gas equilibrium from the "explosion" state (by decreasing T) should not affect the CO concentration appreciably when CH_4 and HCN are present in the gas mixture. The failure to freeze the water gas equilibrium completely is reflected, however, in low CO_2 and high H_2O in the experimental data. CH_4 will exist in relatively large amounts only because the pressure is very high. One would expect the pressure to drop more rapidly than the temperature, after detonation, because of the co-volume effect, so that CH_4 would tend to decompose into C and H_2. HCN would tend to decompose as the temperature decreases. Both effects would result in high C and H_2 concentrations as observed. Since NH_3 is very sensitive to H_2 concentrations, one accounts for the excess NH_3 found experimentally on the basis that it formed during the decomposition of CH_4 and HCN.

Table V lists results calculated by the fugacity and partial pressure methods. When the temperature is high and/or the oxygen balance is quite negative the two calculations lead to quite different results. However, as the oxygen balance approaches zero the differences become less, and, if the "explosion" temperature is also low the difference between the partial pressure and the fugacity methods is negligible at or near zero O.B.

[14] A. Haid and A. Schmidt, Zeits. ges. Schiess-Springstoffw. **26**, 253, 293 (1931).

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

The Vapor Pressure and Heat of Sublimation of Graphite

L. H. LONG
Washington Singer Laboratories, University College, Exeter, England
August 31, 1948

IN a recent communication under the above title, Brewer, Gilles, and Jenkins[1] describe an equilibrium effusion method for measuring the vapor pressure of graphite. From the results of experiments below 3000°K they conclude that the vapor reaches a pressure of one atmosphere at 4630°K, and that the heat of sublimation is 170 kcal./g-atom.

However, apart from the fact that several indirect lines of evidence discussed elsewhere[2] will not admit of the latter value, these figures encounter a number of serious difficulties when compared with much evidence of a more direct nature, as pointed out below:

(i) Setting aside experiments involving the temperature of the positive crater in the carbon arc, which do not give consistent results, there are only three other sets of experiments in which equilibrium temperatures and pressures are measured for graphite. The results of two of these, namely, those of Thiel and Ritter[3] (first two of the three methods described) and Basset,[4] provide temperature-pressure data closely supporting the figure 125 kcal./g-atom for the heat of sublimation (the lowest alternative considered by Brewer *et al.*). The third, due to Ribaud and Bégué,[5] is in poor agreement with the other two and indicates a lower vapor pressure; but in all three cases the vapor-pressure data are higher than those of Brewer *et al.* by several powers of ten.

(ii) Basset[4] found the coordinates of the triple point of carbon to be 4000°K and 100 atmospheres, below which pressure the carbon sublimed without melting. Even if, as Brewer *et al.* suppose, the temperature measurements of Basset are seriously in error, the same is not likely to be true of his pressure measurements. Further, the pressure at the triple point has been independently determined by Steinle[6] who also finds that it is 100 atmospheres. Both Basset and Steinle provide photographic evidence for their conclusions. But, according to the temperature-pressure relation of Brewer *et al.*, the vapor pressure reaches 100 atmospheres above 6000°K. This would place the melting point of graphite at an impossible figure well above those of the refractory metal carbides, whereas, for example, graphite can be fused in a crucible of tantalum carbide which has a reputed melting point of 4150°K. Other experimental figures for the melting point of graphite are variously given as 3800,[7] 3900,[8] 3760,[9] and 3845°K.[10] It thus does not appear that Basset's figure is an underestimate, nor can it be presumed that all of the various investigators cited here have erred in their temperature measurements by such an enormous and approximately constant amount.

(iii) If the vapor pressure of graphite reaches 1 atmosphere at 4630°K, it is surprising that temperatures reported for the positive crater of the carbon arc, which are generally regarded to be limited by the vapor pressure, are never sensibly above 4000°K, even under elevated pressures.

(iv) Apart from absolute temperature measurements, Mott[11] has determined the relative volatilities of a number of substances by a variety of methods. His placing of carbon offers support to the measurements of Basset and of Thiel and Ritter, but is decidedly out of harmony with those of Brewer *et al.*

The consensus of opinion is thus that graphite possesses a very much higher vapor pressure and consequently lower heat of sublimation than Brewer *et al.* affirm. It is relevant to note in conclusion that these authors in their experiments with replaceable graphite tubes found that rapid volatilization occurred which limited the life of the tubes. This observation is scarcely compatible with their own temperature-pressure relation, which in all cases necessitates pressures well below 0.1 mm at the temperatures of their experiments.

[1] L. Brewer, P. W. Gilles, and F. A. Jenkins, J. Chem. Phys. **16**, 797 (1948).
[2] L. H. Long and R. G. W. Norrish, Proc. Roy. Soc. **A187**, 337 (1946); L. H. Long, forthcoming paper.
[3] A. Thiel and F. Ritter, Zeits. f. anorg. Chemie **132**, 125 (1923).
[4] J. Basset, J. Phys. Radium (vii) **10**, 217 (1939); Chimie et Industrie **46**, No. 3b, 7 (1941); Brennstoff-Chemie **23**, 127 (1942).
[5] G. Ribaud and J. Bégué, Comptes Rendus **221**, 73 (1945).
[6] H. Steinle, Zeits. f. angew. Mineralogie **2**, 344 (1940).
[7] K. Fajans and E. Ryschkewitsch, Naturwiss. **12**, 304 (1924); E. Ryschkewitsch, Zeits. f. Elektrochemie **31**, 54 (1925).
[8] A. Hagenbach and W. P. Lüthy, Naturwiss. **12**, 1183 (1924).
[9] H. Alterthum, W. Fehse, and M. Pirani, Zeits. f. Elektrochemie **31**, 313 (1925).
[10] E. Ryschkewitsch and F. Merck, Zeits. f. Elektrochemie **32**, 42 (1926).
[11] W. R. Mott, Trans. Am. Electrochem. Soc. **34**, 255 (1918).

Elution Equations for Adsorption and Ion Exchange in Flow Systems

NEVIN K. HIESTER AND THEODORE VERMEULEN
University of California, Berkeley, California
September 7, 1948

ELUTION, the process of separating from a granular adsorbent bed one or more components previously adsorbed upon it, is an essential step in any regenerative cycle of ion exchange, chromatography, or gas adsorption.

The typical "elution bell" i.e., the concentration-time curve which displays a maximum, has been fitted approximately by the stepwise-discontinuous method of equilibrium stages.[1–3] For the special case where the bed is initially fully saturated, Thomas[4] has provided exact kinetic

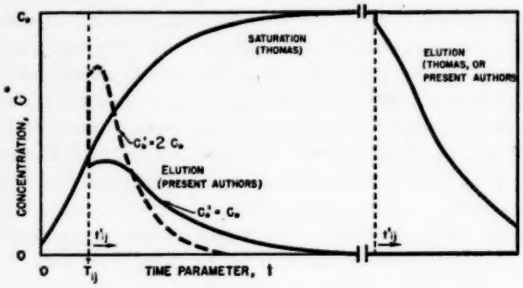


FIG. 1. Concentration curves for a saturating component in an eluting fluid stream passing a given cross section of granular bed; calculated from Eq. (4).

equations which include the result of Boyd, Myers, and Adamson.[5] By an extension of Thomas's method, we have now derived general kinetic equations for the elution bell for any fractional extent of previous saturation.

Our study has shown, incidentally, that Thomas's equations for saturation of an initially empty bed[6] contain the equations proposed by several other investigators. For the concentrations of saturating component in the fluid (c) and on the bed (p), Thomas obtained

$$\frac{c}{c_0}=\frac{\varphi(t,\tau s)+I_0(2(\tau s t)^{\frac{1}{2}})}{\varphi(t,\tau s)+I_0(2(\tau s t)^{\frac{1}{2}})+\varphi(s,\tau t)}, \qquad (1)$$

$$\frac{p}{p_\infty}=\frac{\varphi(t,\tau s)}{\varphi(t,\tau s)+I_0(2(\tau s t)^{\frac{1}{2}})+\varphi(s,\tau t)}, \qquad (2)$$

where we utilize his notation except for τ, s, t, and p_∞ which have the values given in Table I. Only when $\tau=1$ can c/c_0 and p/p_∞ be evaluated exactly from the heat-transfer charts of Furnas.[7] The functions $F(c, p)$ in Table I contain in each case the rate constants for a second-order forward-second-order reverse reaction (typified by exchanging ions of equal valence). For kinetically simpler cases, the constant factors (k_1a) or (k_2c_0) must be replaced in the tabulated terms by whatever rate constants are appropriate.

Consider now that a fluid containing a single saturating component at concentration c_0 has passed through the bed during a time interval, τ_{sat}, which corresponds to a particular value of y and thus of $t_{ij}(=T_{ij})$. At this instant, an eluting fluid (the same fluid, but without saturating component) begins to pass through the bed at an unchanged rate of flow. (For ion exchange, the fluid is assumed to contain an eluting component identical with the species on the bed prior to saturation; its concentration will temporarily be taken equal to that of the saturating component, c_0, in the preceding fluid.)

The equations for elution will depend, first, upon the bed concentration at each point at passage of the (assumedly sharp) new fluid front. Thus at $y'=(\tau'-l/R)/m=0$, where τ' is time reckoned from the start of regeneration, we have

$$\frac{p}{p_\infty}=\frac{\varphi(T,\tau s)}{\varphi(T,\tau s)+I_0(2(\tau s T)^{\frac{1}{2}})+\varphi(s,\tau T)}. \qquad (3)$$

In addition, since the component of interest is no longer entering the bed, $c=0$ at $x=0$. Thomas's conservation and

TABLE I. Rate, distance and time parameters for Thomas equations.

Reaction order		Rate, $F(c, p)$	p_∞	Dimensionless parameters			Previous investigators
Forward (i)	Reverse (j)			τ_{ij}	s_{ij}	t_{ij}	
Surface reaction controlled							
2	2	$k_1c(a-p)-k_2p(c_0-c)$	a	k_2/k_1	mk_1ax	mk_1c_0y	a
2	1	$k_1c(a-p)-(k_2c_0)p$	$\frac{k_1a}{k_1+k_2}$	$\frac{k_2}{(k_1+k_2)}$	mk_1ax	$m(k_1+k_2)c_0y$	b
2	0	$k_1c(a-p)$	a	0	mk_1ax	mk_1c_0y	c–f
1	1	$(k_1a)c-(k_2c_0)p$	$\frac{k_1a}{k_2}$	1	$m(k_1a)x$	$m(k_2c_0)y$	b, e
1	0	$(k_1a)c$	—	1	$m(k_1a)x$	0	g
Diffusion controlled							
1	1	$k_D\left(\frac{k_1a}{k_2c_0}c-p\right)$	$\frac{k_1a}{k_2}$	1	$mk_D\frac{k_1}{k_2c_0}ax$	mk_Dy	h–j

[a] See reference 6.
[b] See reference 4.
[c] G. S. Bohart and E. Q. Adams, J. Am. Chem. Soc. **42**, 523 (1920).
[d] L. G. Sillen, Arkiv. f. Kemi. Min. Geol. **A22**, No. 15 (1946).
[e] J. E. Walter, J. Chem. Phys. **13**, 332 (1945).
[f] Danby, Davoud, Everett, Hinshelwood, and Lodge, J. Chem. Soc. **68**, 918 (1946).
[g] Drew, Spooner, and Douglas: D. M. Klotz, Chem. Rev. **39**, 241 (1946), reference 10.
[h] See reference 5.
[i] O. A. Hougen and W. R. Marshall, Chem. Eng. Progress **43**, 197 (1947).
[j] R. H. Beaton and C. C. Furnas, Ind. Eng. Chem. **33**, 1500 (1941).

rate conditions are then applied, with replacement of y by y', and lead to the equations:

$$\frac{c}{c_0}=\frac{e^{-T}[\varphi(T+t', rs)+I_0(2(rsT+rst')^{\frac{1}{2}})]-[\varphi(t', rs)+I_0(2(rst)^{\frac{1}{2}})]}{e^{-T}[\varphi(T+t', rs)+I_0(2(rsT+rst')^{\frac{1}{2}})+\varphi(s, rT+rt')]+[\varphi(rt', s)-\varphi(t', rs)]}, \quad (4)$$

$$\frac{p}{p_\infty}=\frac{e^{-T}[\varphi(T+t', rs)]-[\varphi(t', rs)]}{e^{-T}[\varphi(T+t', rs)]+I_0(2(rsT+rst')^{\frac{1}{2}})+\varphi(s, rT+rt')+[\varphi(rt', s)-\varphi(t', rs)]}, \quad (5)$$

where r and s remain as before, and t'_{ij} corresponds to the values of t_{ij} in Table I with y replaced by y'. Figure 1 presents typical elution curves as calculated from these equations, with r_{ij} and s_{ij} constant. At large T the equations become identical with those of Thomas,[4] as is indicated in the figure; for instance:

$$\frac{c}{c_0}=\frac{\varphi(rs, t')}{\varphi(rs, t')+I_0(2(rst')^{\frac{1}{2}})+\varphi(rt', s)}. \quad (6)$$

As the new fluid front travels down the bed, the discontinuity in c/c_0 decreases and rapidly becomes negligible; in actual practice, it may be obscured by diffusional effects even at small distances. For ion exchange, the above equations may be extended to regenerant concentrations other than c_0 (i.e., c_0') by replacing c_0 by c_0' (except in the calculation of T which is a "memory" term); in this case a discontinuity is always encountered at the front. Figure 1 shows also how regeneration time is reduced by doubling the concentration level of regenerant.

The curve for p is continuous, but otherwise of the same general shape as for c; its maximum represents a true equilibrium condition, at the time that net reaction at that particular cross section finally shifts from saturation to elution.

Where $r=1$, Eqs. (4) and (5) take on an especially simplified form:

$$\frac{c}{c_0}=e^{-(T+t'+rs)}[\varphi(T+t', rs)+I_0(2(rsT+rst')^{\frac{1}{2}})]-e^{-(t'+rs)}[\varphi(t', rs)+I_0(2(rst)^{\frac{1}{2}})], \quad (7)$$

$$\frac{p}{p_\infty}=e^{-(T+t'+rs)}[\varphi(T+t', rs)]-e^{-(t'+rs)}[\varphi(t', rs)]. \quad (8)$$

The two terms in each of the above equations represent pairs of values in the Furnas charts that are displaced along the t' scale by a value of T.

Saturation and elution equations have also been derived for cases involving more than one "memory" term. We are preparing tables of φ to facilitate exact evaluation of the above equations, and also are charting solutions of Eq. (1) for values of r other than unity. Complete derivations will be reported and applications discussed in a forthcoming paper.

[1] A. V. P. Martin and R. L. M. Synge, Biochem. **35**, 1358 (1941).
[2] S. Stene, Arkiv. f. Kemi. Min. Geol. **18**, No. 18 (1945).
[3] S. W. Mayer and E. R. Tompkins, J. Am. Chem. Soc. **69**, 2866 (1947).
[4] H. C. Thomas, Annals N. Y. Acad. Sci. **49**, 161 (1948).
[5] G. E. Boyd, L. S. Myers, Jr., and A. W. Adamson, J. Am. Chem. Soc. **69**, 2849 (1947).
[6] H. C. Thomas, J. Am. Chem. Soc. **66**, 1664 (1944).
[7] C. C. Furnas, Bur. Mines Bull. **361** (1932); Trans. A.I.C.E. **24**, 142 (1930).

Absorption Spectrum of Hexavalent Plutonium

R. H. Betts and B. G. Harvey
Atomic Energy Project, National Research Council, Chalk River, Ontario, Canada

September 7, 1948

THE chemical similarity between uranium and plutonium now appears to be firmly established.[1,2] Recently, Kasha[3] has used this analogy to explain certain features of the absorption spectrum of PuO_2^{++} in $0.1N$ perchloric acid. Now the absorption spectrum of UO_2^{++} is well known;[4] it contains eleven regularly spaced bands in the region 3400–5000A. These bands are believed to arise from symmetrical vibrations in the U−O bonds of

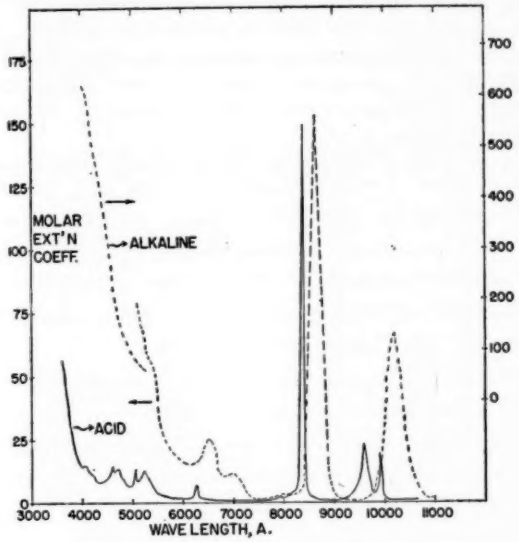


FIG. 1. Absorption spectrum of Pu(VI).

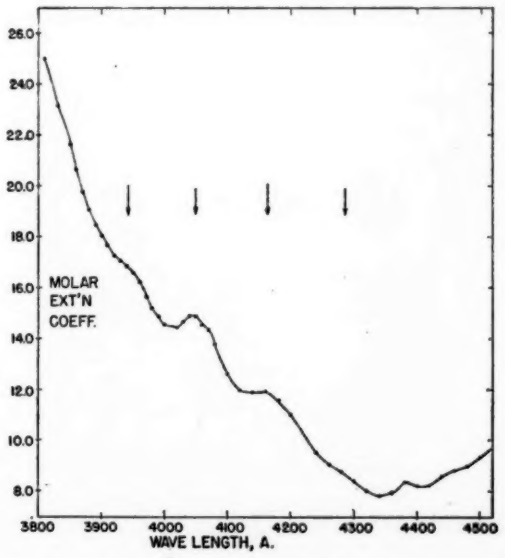


FIG. 2. Absorption spectrum of Pu(VI) in HNO_3 solution.

the UO_2^{++} ion. Kasha found a series of four regularly spaced bands for PuO_2^{++} in the region 3900–4300A, and ascribed them to symmetrical vibrations in the Pu−O bonds. In addition, an exceedingly sharp band at 8330A was found, which was attributed to electronic transitions within the $5f$ electron shell. The UO_2^{++} spectrum has no corresponding sharp lines; this is to be expected, since uranium contins no $5f$ electrons in this valence state.[2]

We have measured the absorption spectrum of PuO_2^{++} in $0.9N$ nitric acid solution, using a Beckman quartz spectrophotometer. The spectrum over the region 3600–10,000A is shown in Fig. 1. This result is very similar to that described for PuO_2^{++} in $0.1N$ perchloric acid.[3] That portion of the spectrum ascribed by Kasha to vibration is shown on an enlarged scale in Fig. 2. Four regularly spaced bands may be distinguished in the region 3900–4300A (indicated by arrows). Starting from the ultraviolet end, the successive frequency intervals for these bands are 630, 670, and 670 cm^{-1}, giving an average of 657 cm^{-1}. This agrees within experimental error with the value of 708 cm^{-1} found by Kasha.[3]

A qualitative comparison of the uranyl and plutonyl spectra at higher pH values tends to confirm this distinction between the vibrational and electronic portions of the Pu(VI) spectrum. For U(VI), Sutton[4] has shown that as the pH is raised above 2.0, the banded structure gradually disappears, and is replaced by a region of more or less continuous absorption below 5000A. We have determined the absorption spectrum of Pu(VI) in dilute ammonium hydroxide solution. (Ammonium plutonate is insoluble, in general, in dilute ammonium hydroxide solution, but we have found on occasion that a solution of Pu(VI) deepens to an orange color on addition of excess ammonia without the appearance of a precipitate.) The result is given in Fig. 1. The peak at 8330A is broadened slightly, and shifted to longer wave-lengths, without a marked change in the extinction coefficient. However, the band structure has been replaced by a region of general absorption with much higher values of the extinction coefficients.

[1] Harvey, Heal, Maddock and Rowley, J. Chem. Soc. 1010 (1947).
[2] B. G. Harvey, Nucleonics **2**, 30 (1948).
[3] M. Kasha, MDDC-591, U. S. Atomic Energy Commission, Oak Ridge, Tennessee (and references therein).
[4] J. Sutton, Report No. 1612, National Research Council of Canada, Ottawa, Canada.